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REUSE AND AIR CLASSIFICATION OF BIOASH

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 18 November, 2015.

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Abstract of master's thesis

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Abstract

The amount of biomass ash (BA) produced worldwide is expected to increase in the near future because biomass is commonly regarded as a carbon neutral fuel. Therefore, sustainable methods for the utilization of BA will be needed to manage the increased flux of BA from the energy sector while concurrently dealing with a smaller allowance of BA that can be landfilled. Therefore, research into new technologies is needed to find and exploit methods to utilize BA in safe and economically and environmentally sustainable ways in order to maximize the environmental benefits of biomass combustion.

Presently BAs are utilized primarily in the construction of landfills or disposed of in landfills, with a minor percentage recycled for various purposes. Viable alternatives to landfill construction and landfill disposal require supportive evidence for their practicality, which is currently limited. One of the main barriers to reuse is the presence of heavy metals in BA. Therefore, finding effective methods for isolating and removing heavy metals is important to allowing reuse and is pursued in this work. Furthermore, this thesis seeks to assess the quality of specific BA samples as the quality pertains to their final usage, and to assess the sustainability of the usage solution to the comparable product that BA is replacing. Technologies were evaluated for their suitability and feasibility for utilizing BA as a replacement for traditional natural resources in specific applications. This thesis will seek to clarify the usage of air classification for refining BA for reuse as a product with the goal of contributing to the knowledge of viable and sustainable solutions for the reuse of BA.

Background information on the quantities, quality, formation, analytical methods, utilization options, treatment methods and law and regulation related to BA were investigated prior to the experimental design. Based on that research and the interests of Ekokem, evaluation of three BA samples for reuse in agriculture, earth construction, cement and landfill disposal was completed. Additionally, air classification tests were performed on the BA samples with the objective of isolating certain components of the BA in a separate fraction; those samples were also evaluated for the same reuse schemes.

The experiments produced three types of results. First was the procedure development in how to carry out air classification experiments and results directly related to air classification that can guide future research. Second were the results for individual samples and their reuse potential; one sample showed reuse possibilities without refining; the two other samples showed some improvements through air classification with isolation of heavy metals in the fine air classified fraction. Lastly, challenges experienced and additional work related to the reuse of BA and air classification experiments were outlined.

Keywords fly ash, biomass, air classification, industrial solid byproducts

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This work is dedicated to the memory of my beloved aunt, Janice Winstead McBurney, who was a lifelong educator. She was an early influence on me providing countless books, pressing the importance of education and inspiring a search for knowledge in natural sciences at a young age. She was proud that I moved to Finland to pursue a Master's degree, and passed away during the pursuit of this achievement. I believe that her spirit for knowledge is smiling upon this work.

Espoo, XX November 2015

Steven William Voshell

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Abbreviations & Symbols

Al – aluminum

Al_2O_3 – aluminum oxide

Ag – silver

AMD – acid mine drainage

As – arsenic

Au – gold

B – boron

Ba – barium

BA – bioash

BBA – bio bottom ash

Be – beryllium

BFA – bio fly ash

Bi – bismuth

C – carbon

Ca – calcium

$CaCO_3$ – calcium carbonate

CaO – calcium oxide

Cd – cadmium

Cl – chlorine

CO_2 – carbon dioxide

Cr – chromium

Cs – cesium

Cu – copper

ESP – Electrostatic Precipitator

F – fluorine

Fe – iron

FeO – iron (II) oxide

Fe_2O_3 – ferric oxide

GHG – greenhouse gas

H – hydrogen

H_2PO_4 – phosphoric acid

H^+ - hydrogen ion

K_2O – potassium oxide

Li – lithium

LOI – loss on ignition

LQL – lower quantitation limt

Mg – magnesium

MgO – magnesium oxide

Mn – manganese

Mo – molybdenum

MSW – municipal solid waste

N – nitrogen

Na – sodium

Ni – nickel

NO_3^- - nitrate

O – oxygen

P – phosphorus

PAH – polycyclic aromatic hydrocarbon

Pb – lead

PSD – particle size distribution

Rb – rubidium

RPM – rotations per minute

S – sulfur

Sb - antimony

Se – selenium

Si – silicon

SiO_2 – silicon dioxide

Sn – tin

Sr – strontium

TDS – total dissolved solids

Ti – titanium

TOC – total organic/oxidizable carbon

V – vanadium

VFR – vacuum flow rate

Hg – mercury	XRF – x-ray fluorescence
ICP-MS – inductively coupled plasma mass spectrometry	XRD – x-ray diffraction
	Zn – zinc
K – potassium	Zr – zirconium

LITERATURE REVIEW

1 INTRODUCTION

1.1 Background Information

The amount of BA produced worldwide is expected to increase in the near future (see Figure 1) because biomass is commonly regarded as a carbon neutral fuel in the sense that CO_2 released from the burning of biomass will be synthesized into hydrocarbons and O_2 by the growth of new biomass. This is expected to help mitigate climate change effects due to artificially high CO_2 levels in the Earth's atmosphere caused by human activity, in contrast to the combustion of fossil fuels for heat and energy. This demand for bioenergy is driven in part by EU climate change policy calling for 20% reductions in GHG emissions by 2020 compared to 1990 levels and 20% mandatory renewable energy with 10% biofuels by 2020 (CoEC 2008, Vanhanen et al. 2014). Additionally, as part of the EU circular economy policy, a call for the reduction and eventual elimination of landfills has been made. The EU is striving to eliminate landfills by 2030 if possible (European Commission 2014). Thus there will be an increase in BAs while at the same time there will be a demand for dealing with the increased mass flux of BA within global waste management streams. Therefore, sustainable methods for the utilization of BA will be needed to manage the increased flux of BA from the energy sector while concurrently managing the smaller allowance of BA that can be landfilled.

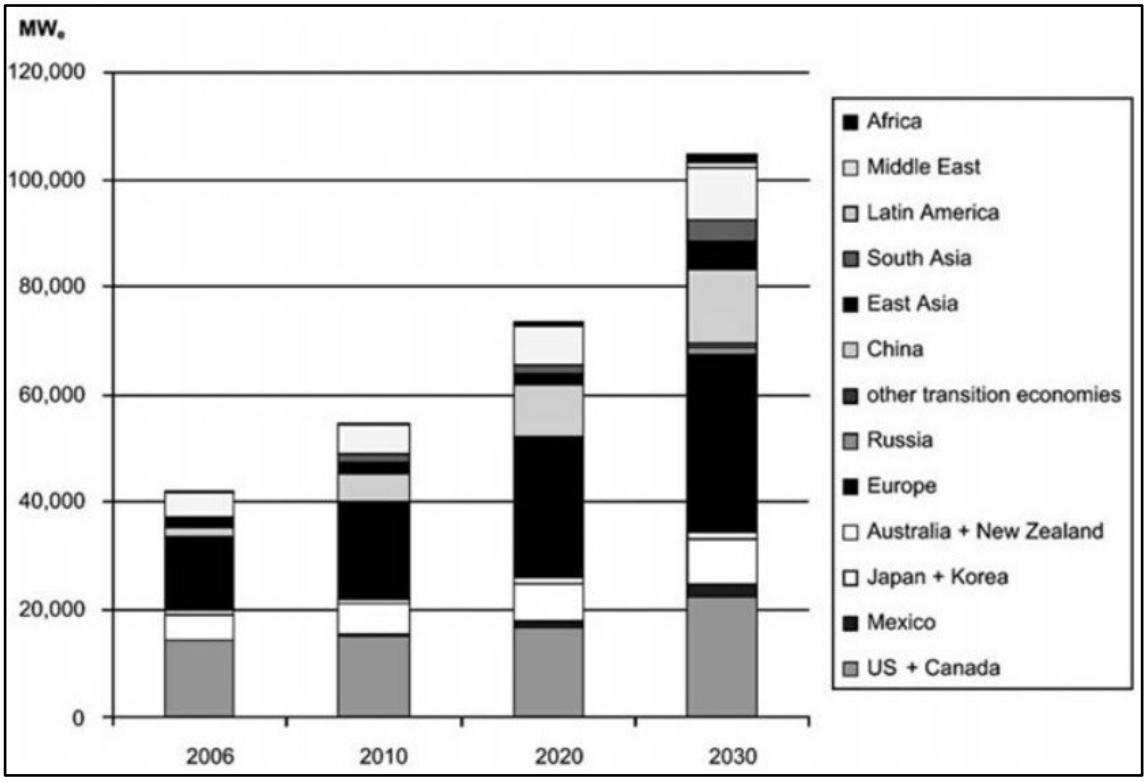

Figure 1: Projected global bioenergy growth and past production (Koppejan et al. 2012).

The need for energy in the Nordic countries is similar to that of other developed nations in Europe and worldwide; however, the need for abundant and reliable heat is in greater demand due to the long and cold winters in this region. The production of heat and energy from biomass is popular in the Nordic countries, and industrial scale biomass combustion is expected to grow in attractiveness in the future, especially due to the available quantity of biomass in this region and inherent carbon neutral status of biomass as an energy source (Knapp et al. 2011). Due to the expected growth in the bioenergy market in the Nordic countries, a proportional growth in the amounts of ashes from biomass combustion is to be expected in the coming years. With this bioenergy growth, a solution to the abundance of BA as a byproduct of heat and energy production is needed, because much of it is currently landfilled or used in the construction and decommissioning of landfills.

Landfilling being widely recognized that the status quo for handling ash is not sufficient to meet the sustainability needs of the future. This is especially true in Nordic countries where governments have planned the elimination or near elimination of landfills; as landfills have been the most cost-effective disposal solution for ashes that

do not have immediate recycling value. This societal problem is coupled with the economic problem of BA costing industry and utilities significant amounts of monetary resources to deal with ash as a waste. The economic benefit would be to transition BA from a waste into a raw material that can be refined, processed and made into a product that could be sold for profit. In doing so this would help reduce the environmental cost associated with landfilling ash. Therefore, research into new technologies is needed to find and exploit methods to utilize biomass ash in economically and environmentally sustainable ways in order to maximize the environmental benefits of biomass heat and energy.

1.2 Research Problem

Presently BAs are utilized primarily in the construction of landfills or disposed of in landfills, with a minor percentage of BAs recycled for various purposes. Viable alternatives to landfill construction and landfill disposal require supportive evidence for their practicality, which is currently limited. One of the main barriers to reuse of BA is the presence of heavy metals in BA. Therefore, finding effective methods for isolating and removing heavy metals is important to allowing reuse.

1.3 Goal

The goal of this thesis is to contribute to the knowledge of viable and sustainable solutions for the reuse of BA. In doing so the current regime of utilizing BA mostly in the construction of landfills will be shifted so that BA utilization will enter a transition stage towards more sustainable usage in one or multiple different targeted uses.

Furthermore, this thesis seeks to assess the quality of specific BA samples as the quality pertains to their final usage, and to assess the sustainability of the usage solution to the comparable product that BA is replacing. Technologies were evaluated for their suitability and feasibility for utilizing BA as a replacement for traditional natural resources in specific applications. This thesis will endeavor to clarify the usage of air classification for refining BA for reuse as a product.

1.4 Scope

The core focus of this thesis will be the study of BA, and the paradigm shift of materials, as it relates solely to BA, from wastes to utilizable raw materials. BA will be defined as the bottom ash and fly ash from the combustion of biomass based fuels, including forestry and agricultural biomass and associated wastes, and peat. BA as it applies to this paper will be defined as the mostly inorganic with a minor organic fraction that make up the solid residues remaining after biomass has been burned. Viable applications for the use of BA will be discussed in addition to methods for analyzing, treating and refining BA.

2 QUANTITIES OF BA

Biomass provides approximately 8-15% of the world's energy, and future estimations expect it to increase to 33-50% by 2050. This equates to more than 7 billion tonnes of biomass, resulting in approximately 476 million tonnes of ash (Vassilev et al. Part 1 2013). The most recent figures available for the quantities of BA produced in Finland reported by Huotari et al. 2015 was approximately 600,000 tonnes of peat and wood ash. It should be noted that some of the data from Huotari is outdated, and ash production data for all facilities in Finland may not be all inclusive.

A decisive source for BA quantities produced in Nordic countries was not found. Therefore, they had to be sourced and filtered from data disseminated from individual countries and separated from data involving MSW ash or coal ash. Therefore, data from the countries of interest is presented below, instead of data from the Nordic countries as a whole.

Ash data collected by the Swedish Ash Programme in 2006 indicates that approximately 561,000 tonnes of BA were produced amongst a total of 1.28 million tonnes of ash per year in 2006 (Bjurström et al. 2009). A newer report from the Swedish Ash Programme summarizing work done between 2012 and 2014 indicated that approximately 1.5 million tonnes of ash are produced per annum in Sweden without indication of BA production numbers. Additionally, the 2012-2014 report predicts that BA production will increase by 250,000 tonnes by 2030 (The Swedish Ash Programme 2012-2014). It is reasonable to think that the increase in ash between 2006 and the 2012-2014 report is due to increased use of biomass and MSW as fuels; as Bjurström et al. indicate in their 2009 report that coal is used sparingly in Sweden.

On a small scale, the quantities of BA produced at a plant or individual boiler may be very dependent on the type of furnace and particulate emission systems cleaning the flue gas. While the total amount of ash produced is dependent upon the fuel, the amounts produced in different ash fractions are very dependent on the combustion technology. Grate fired furnaces, which are typically used in small scale energy production, common in Nordic countries, produce a larger fraction of bottom ash than fly ash. This is often a result of incomplete combustion due to emission reducing combustion parameters, and can leave more unburned carbon in the BAs. Fluidized bed furnaces are common in larger energy production applications which produce greater

than 20 MW of energy. Below this threshold it is generally more cost effective to employ a grate fired boiler (Koppejan et al. 2012). Combustion in a fluidized bed furnace is characterized by near complete combustion of biofuels releasing most of the ash forming particles into the flue gas stream to be collected by particulate recovery systems. The bottom ash from fluidized bed furnaces is typically a mixture of eroded bed material, mainly silicates, and ash. Pulverized fuel systems are also used in large scale applications for biomass combustion, and these furnaces produce more fly ash than bottom ash; however, they are not very common. It is important to realize that these types of furnaces also affect the quality of the ash produced; therefore, quality of BA will be discussed in greater detail in the following section.

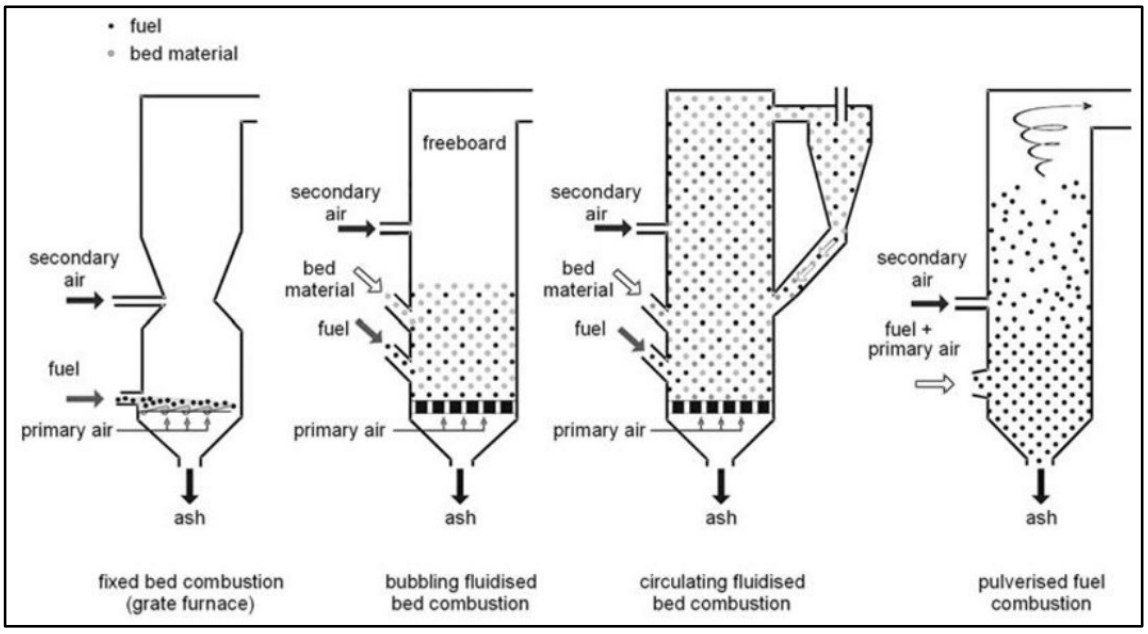

Figure 2: Most common biomass combustion technologies (Koppejan et al. 2012).

3 QUALITY OF BA

The quality of BA is dependent on the fuel from which it originates and several other parameters. A number of factors including the species of biomass, part of the plant or tree, age of the plant or tree, if the is biomass processed, geographical location the biomass originated from, soil type the biomass grew in, harvest season, what type of boiler the biomass was combusted in, contaminants and what type of emission control systems were utilized on the boiler. Due to these characteristics, it is possible that ashes from the same boiler may have significant differences in physical and chemical properties at various times during the year because of dissimilarity in the fuel supply or weather conditions.

Before analysis of the chemical composition of BA it is important to note some of the aspects of its origins which will provide generalities of the chemical composition formed during combustion. Some examples include: agricultural biomass or biomass orginating as the small parts of a plant such as leaves or needles will contain more ash than the wood parts of a plant or tree which have the lowest ash content of all types of biomass. Wood from cooler climates often have less ash, and hardwoods tend to have less ash than softwoods. The temperature at which biomass is burned can have a significant effect on the ash yield, in that higher temperatures may cause the volatilization of ash forming elements, thus presenting more of those elements in the fly ash fraction. The presence of contaminants such as soil or trace additions during processing will affect ash chemistry as well. These characteristics will allow for predictions of ash chemical composition on the basis of the biomass from which it is produced (Vassilev et al. Part 1 2013).

3.1 Ash Formation and Composition

Understanding of ash formation is important in describing the quality of the ash. Three main mechanisms affect the formation of ash: gravity, air entrainment and aerosol formation. In the furnace, gravity will only affect the formation of bottom ash, most notably on particles that are too heavy to be entrained in the flue gas or by the combustion air. This is most pronounced in grate-fired furnaces and less so in fluidized bed or pulverized fuel furnaces (see Figure 3) where gravity is countered by the movement of bed material and flue gas entrainment, respectively. Entrained ash in the

flue gas make up coarse fly ash particles, typically composed of Ca, Mg, Si, K and Al. Within the flue gas, condensation of vaporous species of K, Na, S, Cl and heavy metals on these entrained ash particles occurs. Concurrently, aerosol of CaO is released from the fuel and nucleation and condensation with alkali and heavy metals takes place with the CaO aerosol to produce fine particulates. These mechanisms vary according to the combustion process due to the differences in combustion temperatures, which affect the amounts of volatile elements existing in the separate ash fractions (Koppejan et al. 2012). A diagram of this process is shown in Figure 3. Thus, the quality of BA will be significantly affected by the process and ash fraction, in terms of the major and minor elemental composition.

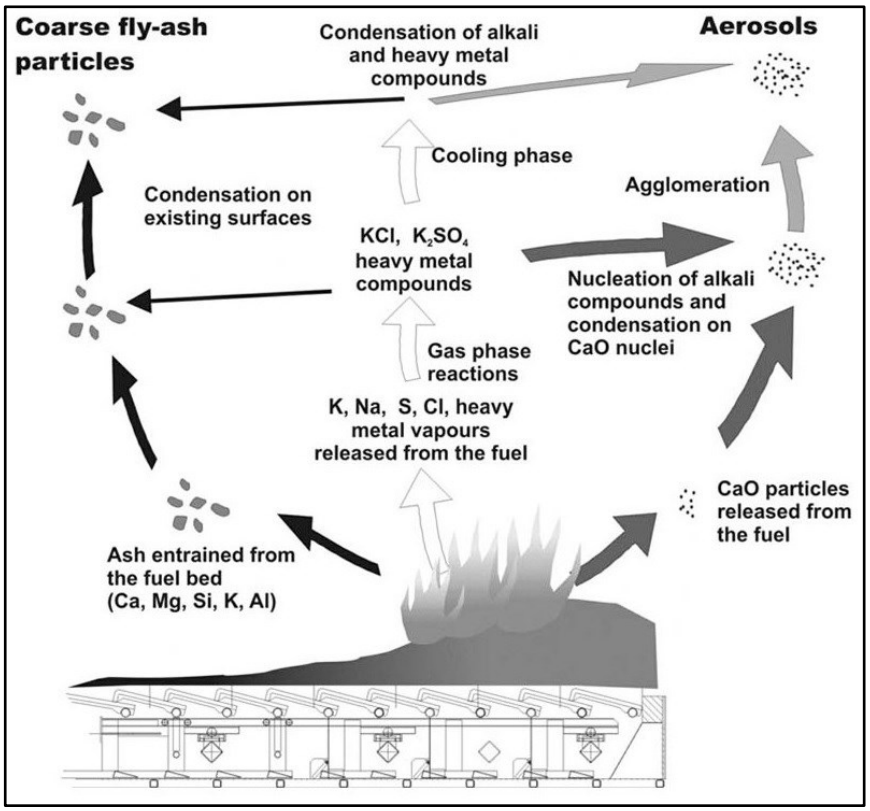

Figure 3: Fly ash formation of wood on in a grate fired furnace (Koppejan et al. 2012).

The type of particulate control devices installed downstream of the furnace affect the quality of fly ash for several reasons. Higher efficiency technologies for particulate capture are preferred to meet emission limits, and inherently they recover a larger fraction of the fly ash mass from the flue gas, often 98-99% or greater. Multiple particulate removal technologies may be used in staged series such as settling chambers

or cyclones in a first stage combined with electrostatic precipitators or bag filters as a second stage. In such a case, the fly ash removed from the first stage will likely have a higher proportion of large particles with a distinct chemical profile and PSD compared to the second stage, which would be characterized by smaller particles and its own chemical and physical profile. The first or second stage particulate controls may also be constructed in series such as multiple cyclones, multiple banks of electrostatic precipitators (ESP) or banks of bag filters.

Despite the marginal heterogeneity of ash, at each level of the series there may be opportunities to isolate concentrated chemical species, and may be of interest for those elements that are most desireable (macro/micronutrients) and undesireable (heavy metals and organic pollutants). It is likely that most fly ash in Finland is from ESPs, and a diagram of a typical ESP is presented as Figure 4.

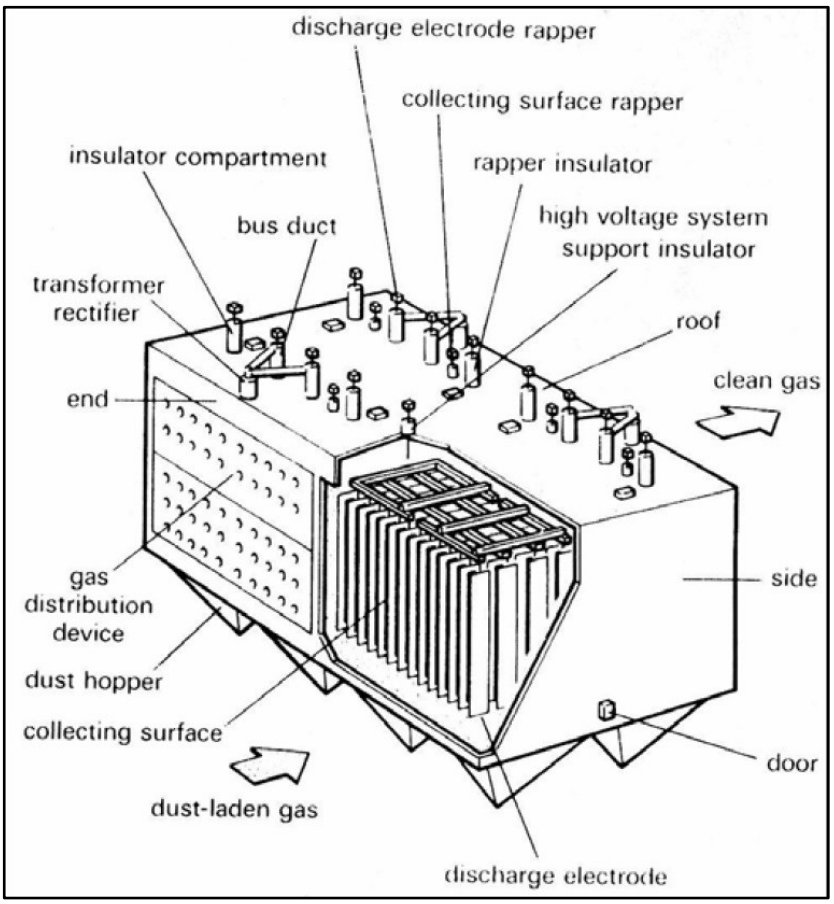

Figure 4: Generic diagram of an ESP (Zevenhoven et al., 2002).

The major elemental components of BA are generally percentage levels of Ca, K, Mg, Si, Al, Fe, and P; mg/kg levels of minor elemental components As, Ba, Be, B, Cd, Cr, Cu, Au, Pb, Hg, Mn, Mo, Na, Ni, Rb, Se, Ag, S, Ti, V, Zn. It should also be noted that O, C and H are typical major elements in BA, they are found as unburned C and chemically bound components to other major and minor elements resulting in oxides, hydroxides, carbonates or other compounds (Karltun et al. 2008; Korpijärvi et al. 2012; Vassilev et al. 2013). These generally inogranic minerals are the bulk of what makes up BA, a comprehensive speciation of these minerals was completed by Vassilev et al. Part 1 in 2013 which identified 229 minerals and chemical phases in a broad study of the composition of BA. Additionally, it should be noted that in the Nordic countries there is concern about the presence of radioactive ^{137}Cs in biomass as a result of the Chernobyl accident in 1986 (Huotari et al. 2015; Bjurström et al. 2009).

3.1.1 Physical Analysis of BA

Physical analysis of BA provides important data that can aid in the determination of BA reuse and if refining or processing is needed. Knowledge of the physical properties of BA samples will allow for comparison of different samples, and comparison of BA against existing products it could potentially replace as a raw material. This also allows for comparison of BA content to legal requirements and technical specifications for potential reuse.

PSD analysis provides a tool to assess the percentage of BA which is present in across a range of particle sizes. Determination of the PSD is typically presented in a graph of particle size versus the cumulative distribution from zero to 100 percent, or in differential distribution where the estimated volume percentage is graphed for each particle diameter. This is informative for heterogenous materials such as BA, because it can allow planning of separation technologies in regard to the particle sizes that need to be managed, and the mass balance analysis of a separated sample. Other descriptive information can be discerned from PSD data such as the mass median diameter and spread of distribution. Mass median diameter being the particle size at 50 percent of the cumulative distribution. Laser light diffraction is typically used to measure PSD, and dry sieving may also be used, but laser light diffraction is better for smaller particle detection (Yeboah et al. 2014).

Density, bulk density and voidage are also interesting physical properties, especially for transporting large quantities of BA or using BA as a geotechnical material. In such cases it may be important to know how BA can be transported, and specifically if aging or processing may increase the density of a particular BA. Density can be defined as the mass per unit of volume of the individual BA particles and can be expected to be between two and three kilograms per cubic meter. Measurement of density can be completed according to standard EN ISO 8130-3. Bulk density is the mass of BA per unit of volume that the BA displaces as a dry solid and can be expected to be less than one kilogram per cubic meter. Measurement of bulk density can be completed according to standard EN ISO 60. Voidage is the volume of space between ash particles and can be calculated as $1 - \rho_{bulk}/\rho_{particle}$ (Lanzerstorfer 2015).

Additional physical analyses can be descriptive in terms of the particle physical characteristics because ash can exist in up to eleven morphological states. The states are defined by the shapes: angular, amorphous, rounded, spherical, vesicular, lacy; and the opacity: non-opaque, opaque or mixed (Yeboah et al. 2014).

3.1.2 Chemical Analysis of BA

The chemical composition of a BA is important to know because it will aid in determining the application the BA can be used with, in addition to providing concentrations of elements that may be controlled by certain regulations. Many different analytical techniques may be applied to BA in order to define its chemical and physical composition. For example, light microscopy, powder x-ray difraction (XRD), differential-thermal, thermo-gravimetric and chemical analyses were all utilized by Vassilev et al. Part 1 2013 to characterize their BA samples. In reviewing the literature these types of analyses appear to be relatively standard for the characterization of BA.

Since the major chemical fraction of BA and ashes in general is inorganic, inorganic chemical analyses may be the most important. When the topic of ash in legislation is covered in detail in Section 6 it is clear that most regulation covering ash is in regards to the total elemental concentrations of inorganic species. Typically, total elemental concentrations in ash or other solids can be quantified accurately with inductively coupled plasma mass spectrometry (ICP-MS). X-ray fluorescence (XRF) is also an effective way to identify the elemental components of solid materials, although

it is not as precise as ICP-MS, nor accepted for important material characterization it can be valuable as a cost effective method for screening elemental composition.

Organic analyses may also be necessary to quantify the amount of char or unburned carbon present in a BA sample. Typically, loss-on-ignition (LOI) or total organic carbon (TOC) (sometimes called total oxidizable carbon) are used to measure the amount of carbon in a BA sample. However, some studies have mentioned TOC analysis is prefered over LOI because LOI can cause loss of volatile inorganics, especially in fly ash, thus giving inaccurate results for unburned carbon contents of a sample (Bjurström et al. 2009). Additionally, if there is a large amount of unburned material as evidenced by the previously mentioned analyses, then it may be necessary to analyze for organic pollutants such as PAHs, dioxins and furans.

As previously mentioned, the quality of BA in terms of chemical composition will affect its usefulness in various applications. Applications of BA will be thoroughly discussed in the following Section 4. Furthermore, utilization of BA is largely based on adherance to regulations of certain chemical components of BA. A thorough study of these regulations in the EU and countries of interest are presented in Section 6.

3.2 Comparison of BA to Coal and MSW Ash

It is worth noting that the breadth of knowledge related to BA as compared to coal ash or MSW ash is fairly limited, because the industrial exploitation of biomass as a fuel has not been as intensive as coal or MSW. Therefore, a brief summary comparison of characteristics for BA, coal ash and MSW ash is included.

First, some generalities when comparing coal ash and BA can be discussed. Primary oxide content ($SiO_2 + Al_2O_3 + Fe_2O_3$) and elements Al, As, Au, Ba, Be, Bi, Cd, Co, Cs, F, Fe, Li, Ni, Pb, S, Sb, Se, Si, Sn, Ti, V and Zr in coal ash are typically at a higher concentration than in BA, while elements such as Ag, B, Br, Ca, Cl, Cr, Cu, Hg, I, K, Mg, Mn, Mo, Na, P, Rb, Sr, Zn are more prolific in BA. Some representative characteristics of BA compared to coal ash are: BA is more water soluble, higher pH, contains more carbonates, chlorides, oxyhydroxides and phosphates while having lower ash-fusion temperatures, lower bulk density, less silicates and fewer sulfates and sulfides. An interesting finding was that coal ash characteristics were not significantly

changed with up to 15% biomass blended in the fuel (Jaworek et al. 2013, Vassilev et al. 2015, Yeboah et al. 2014).

Comparing MSW and BA is a more difficult task because the difference between fuels is much greater than between coal and biomass. The MSW fuel itself if highly variable in content thus producing ash that is highly variable in content. Additionally, ash formation between the two fuel types may differ greatly, because of the combustion process (grate vs. fludized bed vs. pulverized fuel) may be different. Coal being predominantly burned in pulverized fuel furnaces and to a lesser extent fludized bed furnaces; biomass and MSW generally is burned in grate furnaces or fluidized bed furnaces. It is also typical for the generation of high percentages of bottom ash in MSW combustion, while greater percentages of fly ash is typically expected from biomass combustion. Therefore, generalities may be more difficult to support. Major: Si, Al, Fe, Ca, Mg, K, S, P and Cl, and minor forming elements As, Cd, Cr, Cu, Hg, Ni, Pb and Zn are similar, however the total concentrations of metals and heavy metals are expected to be higher in MSW. Heavy metal concentrations in MSW fly ash are found at many times the concentration in BAs. While organic compounds such as PAHs, PCBs, dioxins, furans and chlorinated organic compounds are found at trace levels or are absent from BA, they are routinely found in MSW ash (Lindberg et al. 2015).

4 UTILIZATION OF BA

Utilization of BA is the ultimate goal for industrial BA producers because it has the potential to replace a cost (BA disposal) and liability with a salable product. Minimally, utilization would seek to be a sustainable product with greater expectations of profitability. While much of the ash being produced is utilized already, the utilization scheme is not as sustainable as the future will necessitate. A significant amount of BA is currently used in constructing and decommissioning landfills. In this application, the ash is fulfilling a useful purpose, yet it is still finding its end-of-life-cycle in a landfill. In the EU, it is expected that landfills will be phased out of use, and the EU will be more strictly adhering to the waste hierarchy in the future (European Commission 2014). Therefore, knowledge and expertise will need to adapt to provide technologies with which BA can replace natural resources. In this section, applications for BA that are interesting for future use and development will be outlined and discussed.

Utilization options for ash are numerous, but are limited by economics, legal aspects and practicalities of their applications. Several of the most viable and well-studied applications for BA are highlighted and discussed in this section. The current situation in terms of the use of biomass ash in the Nordic countries appears to be what we could call “productive disposal.” This can be seen in the intensive use of BA in the construction of landfills. While this is currently a solution, in the future the use of landfills will be diminished and other solutions will be needed as a replacement.

4.1 Fertilizer and Soil Amendments

Possibly the oldest use of BA has been as a fertilizer based on the technique of slash and burn agriculture, thus using ash to add nutrients to soil and more importantly to provide a liming effect to acidic soils. From a technical point of view, ash is not a fertilizer because it contains little or no N-compounds. Use of ash as a fertilizer remains relevant today as nutrient depletion from forests and fields is significant when biomass is removed as an energy or food source where otherwise the decay of biomass would have returned these nutrients to the soil. The flux of nutrients away from soils must somehow be repatriated, and using ash to replace lost minerals has been shown to be a viable option. Due to the intensive forestry in the Nordic countries there is a history of returning ash from biomass combustion to the forests from whence the biomass was

produced. Since the early 20th century and intensifying in the 1980s this has been supported by studies showing that minerals extracted by trees during their growth need to be returned to the soil to complete nutrient cycles and encourage increased productivity of forest stands. A significant amount of research has been dedicated to this topic and it is a dominant theme in regard to recycling of ash as can be evidenced in forestry texts: Röser et al. (eds) 2008 and Insam et al. (eds) 2011.

This theme has become particularly true with the use of whole-tree harvesting, which is popular in Nordic countries. In this process, nutrient-rich parts of the tree such as the limbs, top, bark and sometimes the stump and major roots are taken along with the stem from the forest for energy production. During natural processes, the nutrient-rich small branches, top and bark were left in the forest after the tree stem was harvested, and this left much of the trace nutrients extracted during tree growth in the forest to be naturally recycled to the soil (Raulund-Rasmussen et al. 2008).

The semi-closed natural cycles that are interrupted by biomass removal from forests is the soil-flora cation exchange that occurs during biomass growth. Minerals extracted by trees and plants from the soil are exchanged by the plants roots with like-charged ions, and this is generally characterized by base cations such as Ca^{2+}, Mg^{2+}, and K^{+} and acid anions such as NO_3^{-} and $H_2PO_4^{-}$ going to the plant, while the soil receives acid-ions (H^{+}) and the plant builds biomass and releases oxygen gas (Raulund-Rasmussen et al. 2008). This leaves a chemical imbalance between the soil and the biomass resulting in a pH imbalance and acidic conditions in soil until the base ions are returned by the decay of dead biomass. Due to modern forestry practice this process is interrupted because the biomass is removed from the natural system's balance. Therefore, it is postulated that the return of ash from energy production is a viable source of base-cations and P for the remediation of acidic soils and replacement of nutrients (Bjurström et al. 2009; Vassilev et al. Part 2 2013; Karltun et al. 2008).

The use of BA to return minerals to forest soils is also supported by policy; in Sweden use of BA on forest soil is based on "compensation fertilization", where equivalent quantities of minerals are returned to the forest as were removed during harvest. Denmark is a similar case as Sweden, although they merely state that ash may be applied to areas as it is needed. In Finland, ash application is done so that a benefit to the production of wood will be gained (Stupak et al. 2008). However, problems have

been identified with the return of ash to forest soils, and those mainly revolve around two concepts. Firstly, BA may contain elevated levels of heavy metals, which are naturally occurring in biomass, but become more highly concentrated in ash versus biomass. Secondly, some fractions of BA may be deficient of desirable nutrients such as potassium, phosphorus or zinc.

The use of BA as an agricultural lime has potential to replace mined limestone as a raw material. The concerns previously highlighted with regard to BA use on forest soil are of even greater concern in agriculture because of human safety concerns. In Finland, there are limits to some elements in BA that regulate whether or not BA can be utilized in agriculture; however, in Denmark or Sweden comparable agricultural limits were not found (only forestry limits).

It is estimated that direct application of BA to soils may have effective liming potential; however, most newly formed BA have such a high pH value that they may chemically burn ground vegetation or cause a pH shock to the soil. To avoid this situation it is commonly accepted that ash must be treated or aged so that carbonation of the oxides in BA will take place to form mainly hydroxides and carbonates. While not as powerful in terms of liming potential as fresh BA, the aged BA has some preferable characteristics. The aging process typically causes hardening and ash becomes granular and less prone to be dusty, thus safer for handling. The granular state also allows for prolonged dissolution of ash into the environment.

4.2 Cement and Concrete

The production of cement and concrete with coal ash has been studied extensively, and BA to a more limited extent. Replacement of Portland cement with refined BA could be a significant possibility because of the similarities in chemical composition of both materials as well as the continued demand for such products. A comparison of the typical components of Portland cement and BA types which are most relevant to the purposes of this thesis are presented in Table 1. Many BAs have high concentrations of CaO in various mineral forms, which in cement is produced by the energy intensive process of calcining limestone. From the table it can be seen that BA are not totally the same as Portland cement, but have such a similar chemistry that with some refining or blending a product with almost identical composition could be

produced. The presence of elevated K concentration in BA should be noted because the presence of high K concentrations has been linked to loss of compressive strength in cement, and should be avoided (Maschio et al. 2011). Referencing Table 1 for concentrations of K in BA it can be seen that the presence of K in BA could make all BAs unsuitable for extensive use in cement, even those with minimum concentrations of K. Fortunately, a large portion of K compounds in BA are water soluble. A mean of 44% by weight of the K in 26 samples was water soluble, with a maximum of 98.1% of the K in a water soluble form. Therefore, K along with other problematic elements such as Cl, S and Na may be easily washed from BA (Vassilev et al. Part 1 2013; Berra et al. 2015).

Particle size is an important consideration when planning to utilize BA as part of cement or concrete. BA with large particle size and low carbon content has potential for use as an aggregate in concrete that could replace sand or other mined aggregates, while smaller more reactive particles in the ash may work well as a replacement for Portland cement. Maschio et al. 2011 demonstrated with PSD that BFA had a particle size curve very similar to cement, while BBA had a curve similar to sand used in concrete.

Investigations using BA in concrete have shown that concrete formulated with some BA has performed as well or better than concrete made with coal ash or without ash altogether, and they have also presented environmental performance equal to concrete without fly ash in terms of leaching (Barbosa et al. 2013). However, despite the acceptable performance of concretes containing BA, it is often very difficult to meet the EN 450 standards for the chemical composition of the concrete (Berra et al. 2015).

Table 1: Portland cement composition compared to BA composition (Bjarte Oye 2012, Vassilev et al. 2013).

Oxide	Portland cement typical compsition range (wt%)	Wood and woody biomass ash (28 samples)			Peat ash	All Varieties of BA (86 samples)		
		Max %	Mean %	Min %	%	Max %	Mean %	Min %
CaO	60-67	83.46	43.03	5.79	9.97	83.46	25.27	0.97
SiO_2	17-24	68.18	22.22	1.86	37.53	94.48	29.76	0.02
Al_2O_3	4-7	15.12	5.09	0.12	20.14	53.53	5.51	0.10
Fe_2O_3	1.5-5	9.54	3.44	0.37	13.84	36.27	4.00	0.22
MgO	1-5	14.57	6.07	1.10	2.14	16.21	5.42	0.19
SO_3	0.5-3.5	11.66	2.78	0.36	12.11	14.74	3.28	0.01
K_2O	0.2-1.5 (K_2O+Na_2O)	31.99	10.75	2.19	1.12	63.90	17.91	0.16
Na_2O		29.82	2.85	0.22	0.10	29.82	2.48	0.09

4.3 Earth Construction Material

Possibilities exist for the use of BA as a geotechnical material to replace mined materials. One of the main focuses of research has been the construction of road-base with BA, because BA has similar geotechnical properties as the materials traditionally used for this purpose. Relevant studies have investigated the use of BA in construction of low-traffic forest roads which do not have as intensive load-bearing and flexural properties that paved roads entail (Bjurström et al. 2009; Korpijärvi et al. 2012; Ribbing 2007).

Some other geotechnical applications exist that have potential for utilizing BA, such as non-load bearing dry fill material, flowable fill and soil stabilization; however, adequate references to the successful use of BA in these applications was not found. One product in Finland that should be noted is Fill-R® which is a geotechnical rock-like material used in road construction and made with ash (www.smarterthanrock.fi).

4.4 Activated Carbon, Zeolites or Other Adsorption Substrates

Potential for the use of BA as a raw material for the production of activated carbon, zeolites and other adsorption substrates exists, although it has not been studied to the extent that coal ash has for these applications. Ahmaruzzaman 2010 gives detailed summaries of coal fly ash use in applications such as flue gas treatment, wastewater treatment and zeolite production. This review of many studies found that ash has applications in the removal of a variety of pollutants in gas and liquid phase industrial waste streams. Further discussion was applied to the production of zeolites from coal fly ash, which would have the environmental benefit of replacing naturally extracted minerals. The zeolites would have environmental remediation applications as they are excellent adsorbents. The downside of producing zeolites from BFA appears to be the intensive processing involved in their production, which may cost more than extracting them from natural sources. Finally, this technology is not fully mature for BA and requires serious research before it will be feasible.

4.5 Bricks, Glass, Ceramics and Composites

The production of solid materials such as bricks, glass, ceramics or other solid composites have been studied with coal ash, and it is expected that BA could similarly be applied to the manufacture of such products. The production of glass, ceramics and composites are discussed in various literature, but are typically limited to utilization of MSW or coal ash. However, one study was found that incorporated sugar case bagasse ash into a glass-ceramic material with a potential for use as a decorative and durable marble-like product (Teixeira et al. 2014). While the application is promising for future research and as another utilization option, glass, ceramics and composites are not expected to be a bulk consumer of fly ash.

Bricks have the potential to be a large consumer of ash as a raw material; however, there is a similar shortage of applicable literature with regard to their production using BA. It has been demonstrated that production of bricks from ash is a viable and extensively studied with coal ash (Ahmaruzzaman 2010). One study was found during this literature review which utilized BA in brick production (Fernández-Pereira et al. 2011).

4.6 Unburned Carbon

Measureable quantities of unburned carbon are present in BA and are a result of the incomplete combustion of biomass. The content of unburned carbon is typically in the range of 1-20% of BA. Unburned carbon is commonly found in larger granulometric fractions of BA, and may contain organic pollutants such as dioxins, furans or PAHs. The production of unburned carbon is more prevalent in grate-fired furnaces, and combustion systems with low-NO_x burners which are more typical of coal combustion (Vassilev et al. Part 1 2013, Girón et al. 2013).

The separation of unburned carbon from BA may lead to multiple beneficial ends. Concentrated unburned carbon could be returned to furnaces for energy recovery. This is promising for BA that may contain undesirable concentrations of organic pollutants, because the re-burning of these fractions would result in the thermal destruction of the organic pollutants. Also, since unburned carbon may cause interference in the quality of cement or concrete if ash is used, there can be an added benefit of improving the quality of the mineral fraction of BA. Ultimately, this

technology only has the potential to reduce ash quantities while recovering energy and possibly improving the technical aspects of the mineral fraction of BA, and additional technology is required to deal with the remaining mineral ash.

4.7 Landfill Construction and Decommissioning

The use of BA and other ashes in the construction and decommissioning of landfills has and continues to be an important use for these energy byproducts. Fresh ash is used as a sealing layer in landfills and mine tailings impoundments, because as it absorbs water and CO_2 the ash hardens and then has a very low permeability. This low permeability prevents water and O_2 from entering the landfill body thus preventing the production of landfill leachate or the oxidation of acid-producing compounds. Furthermore, a layer of ash with a high pH effectively prevents the infiltration of plant roots into the landfill body, therefore protecting the sealing layer from being compromised (Bjurström et al. 2009).

While currently a viable technology for the utilization of BA, as previously mentioned, the construction and decommissioning of landfills is expected to greatly decrease in the near future within the EU. Likewise, when ash is used for this purpose it is in effect being landfilled alongside other wastes. Positively in this application, ash is replacing mined natural resources such as clay. For the purposes of this thesis, the utilization of BA as a landfill construction material will not be pursued since it is already a well-studied and utilized technology, and does not have the future market potential and environmental performance sought after in this research.

4.8 Mine Filler

Another use in which ash may be used to replace natural resources is as a mine filler. During the abandonment of old mines cavities there is often a need for a filler that can improve the structural soundness of the mine, thus preventing collapse and surface subsidence. An additional benefit of utilizing ash for this purpose is the remediation and prevention of AMD. AMD is a common problem in mines because of the interaction between groundwater and exposed sulfidic minerals, which leads to low pH and the dissolution of heavy metals. The alkaline characteristics of ash may be able to buffer

these reactions, and after solidification of the ash, prevent or slow the migration of groundwater through the abandoned mine.

In the same way that fly ash slurry can be used to stabilize soils by subsurface injection, the fly ash slurry or dry fly ash may be injected into a mine cavity. Dry ash can be used if it will become hydrated by groundwater within the mine. Hydration speeds carbonation and hardening of the fly ash so that it seals the mine and provides the intended structural support (Ahmaruzzaman 2010).

The technical details above are based on research with coal ash, and sufficient research with BA in this application was not found. However, it is expected that BA would behave similar to coal ash as a mine filler because of its cementitious and alkaline properties.

5 METHODS OF TREATING OR REFINING BA

For the utilization of BA, some treatment to affect the properties of the ash will likely be necessary to produce the desired characteristics of a final product. Treatment can be as simple as storing BA for a prescribed time to induce carbonation, or as complex as chemical separation or high temperature vitrification. Just as dealing with any waste, there is a hierarchy to treatment that should be recognized in terms of the environmental performance and economics of treating combustion residues. The hierarchy is as follows: 1) No treatment, 2) if utilization of the residue is possible, consideration of utilization with minimal treatment (aging or screening/separation), 3) As treatment becomes more extensive it should be proportional to the profitability of the final product, 4) expensive and intensive processes such as washing, leaching, extraction or energy intensive treatments should be avoided unless absolutely necessary (Bjurström et al. 2009). In this section, current technologies and state-of-the-art processes for the treatment of ash will be summarized as it applies to BA in the Nordic countries and the purposes of this thesis.

5.1 Aging, Carbonation and Self-Hardening

Untreated or newly formed ash tends to have alkaline properties, is reactive and will produce a high pH in water; this provides a liming quality that can be utilized in the treatment of acidic soils. In the use of ash as a fertilizer or soil amendment on forest soils a pre-treatment or hardening has been needed to allow the natural conversion of oxides in the ash into carbonates, bicarbonates, hydroxides and other minerals by reactions with CO_2 and water. This hardening of the ash reduces its reactivity and liming properties, but ultimately makes ash safer to handle and allows for more even dissolution and distribution into the forest ecosystem. Without treatment ash could cause chemical burning of vegetation or pH shock to the soil, and dust from untreated ash could pose a health and safety issue to people. Additionally, the decreased surface area of the treated ash along with the alkalinity provides for reduced leaching of trace metals in BA. Hardening can be achieved by addition of water and allowing the natural self-hardening process to occur; however, hardening may be more homogenous with the use of machinery and the addition of water in pelletization or granulation, especially for

large amounts of BA. The downside of mechanical treatment is the cost of machinery, energy and water needed to process ash (Karltun et al. 2008).

5.2 Grinding

Ash may need to be ground into finer particles for certain purposes if it is to be utilized effectively when large diameter fractions of particles have a preferable chemical profile, but are too large for a specific application. This may be needed if ash is used in cement as sometimes material standards require a particle size specification (see Section 4.2). It may be most beneficial to use separation for removal of particles that do not meet size specifications. Maschio et al. 2011 demonstrated that BBA could be milled and screened so that it closely followed the PSD of screened BFA and cement.

5.3 Separation

Separation can be a useful process in the refining of BA because it can allow the upscaling of certain compounds into highly concentrated fractions in order to separate them because they have desirable or undesirable properties. Possibilities for dry separation include mechanical methods such as screening or air classification, or more intensive methods like triboelectrostatic or magnetic separation. Separation is preferred if the reactivity of the ash is to be kept unchanged. If water is added to the newly formed ash then the natural carbonation and hardening processes will be accelerated, and the properties of the ash will quickly change. Separation can also be done by wet methods such as floatation, which may be used effectively to separate unburned carbon. Wet separation such as washing will be covered with chemical treatment in Section 5.4.

A typical reason that separation is used to refine ash is to remove unburned carbon from the mineral portion of ash and concentrate it for energy recovery or other uses. Often times this can be easily achieved because in many types of ash the unburned carbon can be concentrated in larger diameter granulometric fractions of ashes, especially those from grate-fired furnaces (Girón et al. 2013). Recovery of carbon in the form of unburned char can result in a two or three-fold benefit scenario in that it can recover unutilized fuel and return it to the boiler for increased efficiency, simultaneously it can eliminate chemical species such as PAHs, dioxins and furans; or char can be used as a raw material for the production of value added products such as

activated carbon. This separation could also be beneficial to the use of BA in cement and concrete, because the unburned carbon content of the ash may negatively affect their performance characteristics (Berra et al. 2015).

Separation has been shown to be an applicable technology for the separation of particle fractions containing higher levels of heavy metals. Camerani et al. 2002 showed that Cd is enriched in small ash particles in biomass combustion, thus the overall concentration of Cd of a heterogeneous ash could be reduced by eliminating some finer ash fractions. Since the concentration of Cd in BA is often problematic for the reuse of BA, separation of coarse ash fractions for utilization and finer fractions to isolate high concentrations of Cd may be a practical treatment regimen.

5.3.1 Air Classification

Air classification is discussed in greater theoretical detail than other technologies mentioned under the separation heading because of its inclusion in the experimental section of this thesis. A cut-away of an industrial scale air classifier is presented as Figure 5.

Air classification is able to accomplish what sieving cannot effectively complete in separating dry materials at cut points at or below 100 to 300 microns. For industrial scale applications where sieves of small sizes are very fragile and may easily clog, therefore are not feasible for industrial scale dry separation of powdered materials. This becomes more apparent as the particle diameters enter double-digit or single digit micron sizes where only sieving on a laboratory scale is possible.

The principles of air classification are based on the terminal settling velocity of particles, which is the speed at which a particle falls at a constant velocity in air. Since heterogeneous powders like ash have particles of different diameters the different sized particles also have different terminal settling velocities. Therefore, smaller particles can be entrained in moving air and larger particles will fall, thus a separation is achieved. Since the effectiveness of this alone is reduced as particle sizes becomes smaller, then additional forces must be applied to the particles to allow more effective separation. The additional force applied is an increase in gravity by employing rotational motion on the particles and air. The rotational motion multiplies the force of gravity on the particles, and the settling velocities of differently sized particles becomes greatly differentiated.

This yields three important characteristics of air separation: 1) classification can be performed in a small volume, 2) classification of a large amount of material and 3) accurate classification can be achieved.

A constraint of air classification is that in dealing with heterogeneous materials such as ash, there exists solids with differing specific gravities and particles shapes which may affect the ability of an air classifier to make separations at precise cut sizes. An example would be a large particle with a lower specific gravity may be entrained in the classifier with much smaller particles that have a higher specific gravity (Jawale, The DIRK PFA Classification Products).

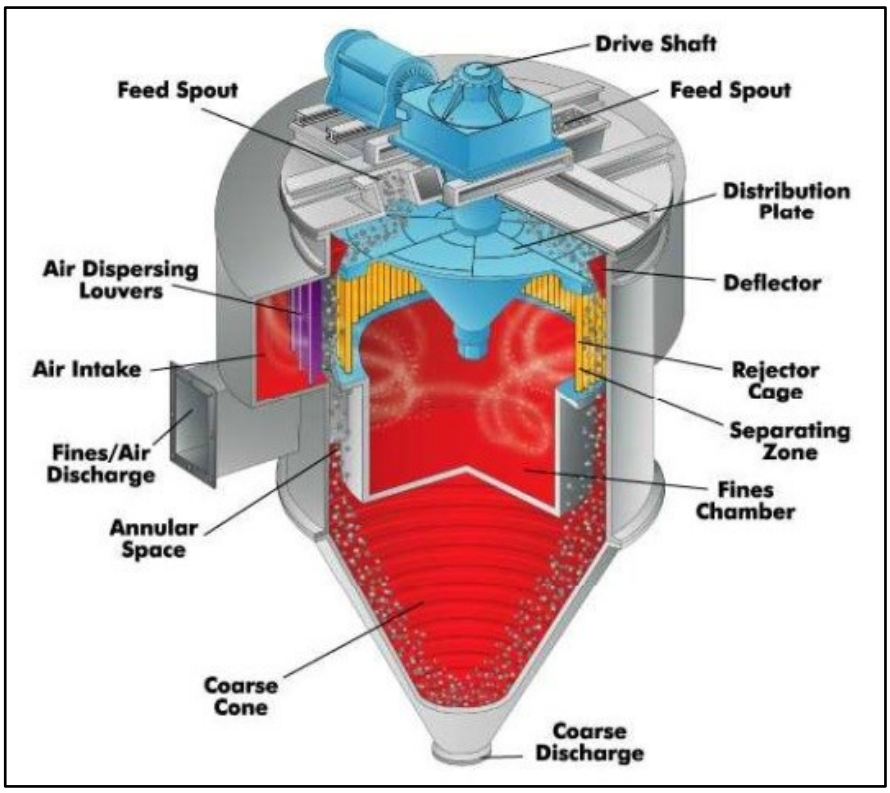

Figure 5: Example of an industrial scale air classifier mechanism (Jawale, The DIRK PFA Classification Products).

5.4 Chemical Treatment

Chemical treatment of ash can be a viable refining method and generally includes washing ash with water, solvent or acid to remove select chemical species. Washing can be an effective method for the removal of salts such as chlorides, sulfates and some alkaline compounds. This may be useful in the treatment of ash for the use in

cement or concrete as chlorides and sulfates can interfere negatively with their strength properties (Berra et al. 2015).

Studies related to the chemical treatment of BA appear to be limited and only three were noted during this literature review. The articles involved the electrodialytic treatment of BA for the removal of Cd, because Cd is often a limiting heavy metal for the reuse of BA. The experimental processes took weeks to complete, but did show promising results for the removal of Cd and other heavy metals (Chen et al. 2015, Kirkelund et al. 2013, Pedersen 2003).

Chemical treatment has downsides due to the use of water or chemicals, which will include added cost to the treatment process. The production of wastewater or chemical waste related to chemical extraction needs to be carefully considered with this process route.

5.5 High-Temperature Treatment

Sintering or vitrification of ash are possible methods for treating ash, although they are often avoided because of the required energy inputs. It should be noted that there is little or no literature regarding the thermal treatment of BA, as no studies were encountered during this literature review. However, the subject has been studied on MSW ash extensively because of the prevalence of heavy metals in these combustion residues and the suitability of the vitrification process in significantly reducing the leachability of heavy metals from ash.

6 LAW AND REGULATION OF BA AND BA PRODUCTS

Laws have a bearing on the reuse of BA because it is regarded as a waste and often contains elements that pose a health hazard to humans and the environment. A review of law and regulation as it applies to BA is important to the study of BA reuse because it will apply to any possible solution. In the following section, law and regulation will be discussed in the EU, the Nordic countries as specified, and others as they apply. Discussion of legislation in Finland was the primary focus of this research because the research done in this thesis is based in Finland. Additionally, mention of relevant legislation in Sweden and Denmark is included due to Ekokem's business presence in those countries.

6.1 Finland

In the following section a summary of Finnish legislation that is applicable or may become applicable to BA is included. Some overlap of EU and Finnish legislation is noted and discussed as appropriate. Some of the applicable legislation includes English translations; however, these English translations are not legally binding according the source (FINLEX). In cases where the English translations are older than the most current legislation it is noted, and the most current legislation at the time of this thesis' writing, as found in the Finnish language versions, is recorded. It should be noted that the author's native language is English with modest capabilities to read and interpret legislation which exists solely in Finnish. Therefore, this section is meant to be a guide or outline of the most current legislation, and only summarized or interpreted those pieces of legislation that were translated into English.

6.1.1 EU Waste Directive and Finnish Waste Law

The EU Waste Directive (98/2008) was adopted by Finland in 2011 and is presented as the Finnish Waste Law (646/2011). Finnish Waste Law also includes amendments 1104/2011, 195/2012, 1178/2013, 25/2014, 410/2014 and 528/2014 which are the most recent at the time this document was authored. The EU Waste Directive provides a waste hierarchy which is implemented to guide industry towards primary material reductions for environmental improvements. The EU Waste Directive articles applicable to ash and ash reuse within the waste directive were summarized below.

Since BA is not considered a by-product it must be handled according to the Finnish Waste Law as specified by the Finnish Environmental Protection Act, which will be discussed later in this text.

Article 4 of the EU Waste Directive and Finnish Waste Act provide guidance as five categories for waste management and prevention of waste:

1. Prevention
2. Preparing for re-use
3. Recycling
4. Other recovery
5. Disposal

Article 5 of the EU Waste Directive and Finnish Waste Law provide additional criteria for the determination of a materials status as a by-product or a waste, it is found verbatim in those documents, and it is written as follows:

1. Further use of the substance or object is certain
2. The substance or object can be used directly without any further processing other than normal industrial practice
3. The substance or object is produced as an integral part of a production process
4. Further use is lawful, i.e. the substance or object fulfills all relevant product, environmental and health protection requirement for the specific use and will not lead to overall adverse environmental or human health impacts.

Article 6 of the EU Waste Directive and Finnish Waste Law provide guidance for the end-of-waste status, in other words, when a waste will no longer be considered a waste under the legislation. The following criteria are as found in the EU Waste Directive; however, the Finnish Waste Law provides one additional criteria, and is written as follows

(1.) The substance or object has undergone a recovery operation (as found in the Finnish Waste Law, but not present in the EU Waste Directive)

1. The substance or object is commonly used for specific purposes
2. A market or demand exists for such a substance or object

3. The substance or object fulfills the technical requirements for the specific purposes and meets the existing legislation and standards applicable to products
4. The use of the substance or object will not lead to overall adverse environmental or human health impacts.

(EU, Directive 2008/98/EC; FINLEX, Waste Act)

The significance of these pieces of legislation are noted because they initially define BA as a waste, and also provides parameters for redefining BA as a raw material. In dealing with BA as a waste or as a raw material it becomes subject to further legislation as follows.

6.1.2 Waste Tax Act

Waste Tax Act version 495/1996 with amendments up to 1066/2002 are translated into English via FINLEX. However, it is known that the Waste Tax Act was previously updated to version 1126/2010, and contains the amendments 651/2011, 970/2012, 534/2014 and 1072/2014.

Currently the tax on waste sent to a landfill is 55 euros per tonne according to the most current amendment (1072/2014). However, BA has been exempt from the landfill tax when it is used in the construction of landfills. This is not expected to continue indefinitely, and it is probable that tax of BA and other ashes used in landfill construction will be taxed in the future (FINLEX, Jäteverolaki 1126/2010).

6.1.3 Environmental Protection Act

Environmental Protection Act version 86/2000, which has been annulled, with amendments up to 1066/2002 are translated into English via FINLEX. However, the Environmental Protection Act was updated to version 527/2014, and at the time of this document's writing, amendments 579/2014, 423/2015 and 802/2015 were included.

As mentioned in Section 6.1.1, when waste meets end-of-waste criteria then it can be managed under the Environmental Protection Act. Therefore, if the material is to be further processed or mixed with other waste an environmental permit must be completed according to this legislation. For the purposes of this thesis, the reuse of BA will necessitate an environmental permit if it is to be made into a new product. According to Pesonen 2012, it may be possible to use ash as a fertilizer or in earthen

construction without environmental permits, but notification to environmental authorities may be necessary (FINLEX, Ympäristönsuojelulaki 527/2014).

6.1.4 Earth Construction

The use of fly ash a bottom ash from coal, peat and wood-based materials (as defined in the legislation) is possible in earth construction according to Government Decree 591/2006 concerning the recovery of certain wastes in earth construction. Additionally, amendments to this degree 403/2009 and 1825/2009 have been issued in Finnish, but do not have English translations in FINLEX. Limit values for chemical constituents in fly or bottom ashes that may be used in earth construction are found in the following Table 2 as presented in Government Decree 591/2006. In addition the document provides guidance for the sampling and analysis of waste materials to be used in earth construction.

Table 2: Limit values for chemical constituents in ash used for earth construction (FINLEX, Government Decree 591/2006).

Harmful Substance	Limit value, mg/kg dry matter Basic characterisations[1]			Limit value, mg/kg dry matter Quality control investigations[1]		
	Content	Leaching (L/S = 10 l/kg) Covered structure	Leaching (L/S = 10 l/kg) Paved structure	Content	Leaching (L/S = 10 l/kg) Covered structure	Leaching (L/S = 10 l/kg) Paved structure
PCB[2]	1.0					
PAH[3]	20/40[4]					
DOC[5]		500	500			
Antimony (Sb)		0.06	0.2			
Arsenic (As)	50	0.5	1.5	50		
Barium (Ba)	3000	20	60	3000		
Cadmium (Cd)	15	0.04	0.04	15		
Chromium (Cr)	400	0.5	3.0	400	0.5	3.0
Copper (Cu)	400	2	6.0	400		
Mercury (Hg)		0.01	0.01			
Lead (Pb)	300	0.5	1.5	300	0.5	1.5
Molybdenum (Mo)	50	0.5	6.0	50	0.5	6.0
Nickel (Ni)		0.4	1.2			
Vanadium (V)	400	2.0	3.0	400	2.0	3.0
Zinc (Zn)	2000	4.0	12	2000		
Selenium (Se)		0.1	0.5		0.1	0.5
Fluoride (F^-)		10	50		10	50
Sulfate (SO_4^{2-})		1000	10000		1000	10000
Chloride (Cl^-)		800	2400		800	2400

[1] Cf. Section 2 in Annex 2.

[2] Polychlorinated biphenyls, total quantity of congenerics 28, 52, 101, 118, 138, 153 and 180.

[3] Polyaromatic hydrocarbons, total amount of compounds (anthracene, acenaphthene, acenaphthylene benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, phenanthrene, fluoranthene, fluorene, indeno(1,2,3-c,d)pyrene, naphthalene, pyrene, chrysene).

[4] Covered structure/paved structure

[5] Dissolved organic carbon

6.1.5 Fertilizer Products Act and Regulation

The most current law regarding fertilizer products in Finland is the Fertiliser [sic] Products Act 539/2006, and is available in English with amendments up to 340/2010. Additionally, in Finnish language texts there are additional amendments, 659/2011, 846/2011, 98/2014, 543/2014, 913/2014 and 520/2015, in existence at the time of this thesis' writing that were not included in the English translation.

Since there is opportunity and need for both agricultural and forestry related fertilizers and soil conditioners that could be made from BA this legislation has significant basis for mention in this document (FINLEX, Fertiliser Product Act 539/2006).

Table 3: Fertilizer limits for elemental constituents.

Element	Unit	Agricultural ash-based fertilizers or raw materials used added to ash	Forestry ash-based fertilizers or raw materials used added to ash	Minimum or maximum elemental concentration
Ca	%	10	6.0	min
P + K	%	2.0	2.0	min
As	mg/kg	25	40	max
Cd	mg/kg	2.5	25	max
Cr	mg/kg	300	300	max
Cu	mg/kg	300	700	max
Hg[1]	mg/kg	1.0	1.0	max
Pb	mg/kg	100	150	max
Ni	mg/kg	100	150	max
Zn	mg/kg	1500	4500	max

1. Mercury analysis by EPA Method 743

6.1.6 Landfill Legislation

Although English translations of the following pieces of legislation were not available they will be mentioned because of the significant role that ash, and especially BA has in the construction and decommissioning of landfills. Government Decrees 861/1997 and 202/2006 define the classification of landfills, i.e. non-hazardous or hazardous (861/1997), the landfill construction parameters (861/1997) and limit values

of waste for determination of landfill classification (202/2006). Government Decree 871/1997 has been amended with the following changes: 1049/1999, 552/2001, 13/2002, 202/2006, 59/2008 and 381/2008. Table 4 presented below summarizes the limit values for landfill waste disposal as inert waste, non-hazardous waste and hazardous waste (FINLEX, Valtioneuvoston päätös kaatopaikoista 861/1997; FINLEX, Valtioneuvoston asetus kaatopaikoista annetun valtioneuvoston päätöksen muuttamisesta 202/2006).

When options for reuse have been exhausted then evaluating the suitability for using ash as a landfill construction or decommissioning material, or as a last resort, disposing of ash in a landfill should be addressed. Therefore, mention of this legislation is included to facilitate this option.

Table 4: Limit values for waste disposal as inert waste, non-hazardous waste and hazardous waste.

Analyte	Limit values (mg/kg) of dry solid for inert waste landfill (L/S = 10 L/kg)	Limit values (mg/kg) of dry solid for non-hazardous waste landfill (L/S = 10 L/kg)	Limit values (mg/kg) of dry solid for hazardous waste landfill (L/S = 10 L/kg)
Arsenic (As)	0.5	2	25
Barium (Ba)	20	100	300
Cadmium (Cd)	0.04	1.0	5.0
Chromium (Cr)	0.5	10	70
Copper (Cu)	2.0	50	100
Mercury (Hg)	0.01	0.2	2.0
Molybdenum (Mo)	0.5	10	30
Nickel (Ni)	0.4	10	40
Lead (Pb)	0.5	10	50
Antimony (Sb)	0.06	0.7	5.0
Selenium (Se)	0.1	0.5	7.0
Zinc (Zn)	4.0	50	200
Chloride (Cl^-)	800	15000	25000
Fluoride (F^-)	10	150	500
Sulfate (SO_4^{2-})	1,000[1]	20000	50000
DOC	500[2]	800	1000
TDS[3]	4000	60000	100000

[1] Waste satisfies the eligibility requirement if the sulfate content does not exceed the following limits: 1,500 mg/L (for the flow-through test, in the first extract at L / D = 0.1 l/ kg) and 6,000 mg/kg
(at L/S = 10 L/kg). To determine the concentration at L / S = 0.1 L/kg the flow-through test must be used. The concentration at L / S = 10 L/kg may be determined either by shaking or
the flow-through test.

[2] If the DOC limit value is exceeded for waste in its own pH, the waste can be alternatively tested at L/S = 10 L/kg at a pH of 7.5-8.0. Waste is considered to satisfy the DOC eligibility requirement, provided that the content is not more than 800 mg / kg.

[3] The limit value of the total amount of solutes can be substituted for the sulphate and chloride limit values.

6.1.7 REACH Legislation

REACH is EU level legislation governing chemicals and potentially hazardous substances, and it does not concern wastes as they are governed under the EU Waste Directive and member states' laws. However, if a substance meets end-of-waste criteria then it is regulated under the umbrella of REACH; thus REACH is significant for the reuse of BA.

REACH Regulation 1907/2006 is the most current legislation with amendments up to 895/2014 included at the time this document was written (ECHA, REACH Legislation).

6.2 Sweden & Denmark

As with Finnish legislation, Swedish and Danish legislation was generally found written in their respective languages. Therefore, information provided in regards to Swedish and Danish legislation was completed to the best abilities of the author to find English translations of Swedish and Danish legislation and interpret them with regards to their application in dealing with BA.

The Swedish Environmental Code (DS 2000:61) gives general guidance for the protection of the environment in Sweden, definitions of waste and provisions for environmental permits that could have bearing on the disposal or reuse of BA. Similar to Finnish legislation, EU directives such as end-of-waste criteria and REACH are also applicable in Sweden according to Bjurström et al. 2009. Some other pieces of Swedish legislation that Bjurström et al. 2009 indicate to have bearing on the governance of BA are: Building Product Directive (EU) (which also exists in Finland), guidelines for contaminated soil (Swedish EPA) and criteria for the utilization of waste as construction material (Swedish EPA).

Danish legislation is likewise greatly shared with EU legislation, in particular, the Waste Framework Directive provides guidance for Danish waste legislation. Ash from wood and peat is found in the EC list and waste in Denmark the same as it is in the European List of Waste (Danish Ministry of Environment, EC list and waste). In Denmark the Environmental Protection Law covers the use of biomass ash and was updated in 2008 with regulation of PAHs.

In Denmark, fertilizer with phosphorus content of 0.1% or more is allowed to contain 110 milligrams of Cd per kilogram of P. However, the Statutory Order does not apply to waste materials such as ash unless P from raw phosphate has been added to the material (Danish Ministry of Environment, Statutory Order on cadmium concentration in phosphorus fertilizer). Therefore, it may be possible to use ash with higher concentrations of Cd than what is shown in Table 5 below. It should be noted that this Statutory Order is dated 5 April 1989 with notation indicating the 110 milligrams of Cd per kilogram of P was in effect after 1 July 1998. It is likely that this legislation may have been superseded since that time. Additionally it was noted by Koppejan et al 2012 that the organic carbon content of ash should be less than 5% for use on agricultural land or forests in Denmark.

Table 5: Limits for elements in ash used for fertilizer in Finland, Sweden and Denmark (Karltun et al. 2008, Nurmesniemi et al. 2012).

			Finland		Sweden		Denmark	
Parameter	Unit		Limit Value		Limit Value		Limit Value	
			Agri/Forest				Straw+mix/wood ash	
Ca	%		10/6.0	min	12.5	min	-	
Mg	%		-		1.5	min	-	
K	%		-		3.0	min	-	
P	%		-		0.7	min	-	
P + K	%		2.0	min	-	min	-	
Zn	%		-		0.05	min		
As	mg/kg		25/40	max	30	max	-	max
B	mg/kg		-		800	max	-	
Cd	mg/kg		2.5/25	max	30	max	5/20	max
Cr	mg/kg		300/300	max	100	max	100	max
Cu	mg/kg		300/700	max	400	max	-	max
Hg	mg/kg		1.0/1.0	max	3.0	max	0.8	max
Pb	mg/kg		100/150	max	300	max	120/250	max
Ni	mg/kg		100/150	max	70	max	30	max
V	mg/kg		-		70	max	-	max
Zn	mg/kg		1500/4500	max	7000	max	-	max

6.3 Other

While having similar properties as coal ash, BA is not included in American standard ASTM C 618 or European standard EN 450-1, which only cover the use of coal ash in the production of cement. It should be noted that the European standard does allow for a maximum of 20% of biomass as a fuel. Fineness of the ash is also regulated

by these standards (Berra et al. 2015). Similarly, standard EN 13055 is a set of requirements for using coal bottom ash in civil engineering (KEMA). A pozzolanicity test can be completed with EN 196-5 test method (Berra et al. 2015).

7 ANALYSIS OF TECHNOLOGIES

An analysis of the studied ash utilization schemes and technical aspects of the manufacture of the products was completed to narrow the possibilities for more detailed research in this thesis, and for guidance towards future research. A table was created with the possible BA products cross-referenced with specific technical aspects of each product which could be ranked on a scale of one to five. Each technical aspect could be weighted so that it could count for more than another if deemed appropriate. The sum of the aspects' ranks were calculated for each product, and the highest ranked products were the best suited for research according to the analysis. The analysis may be viewed below as Table 6.

Table 6: Analysis of available technologies of interest for BA utilization.

	Interest	Production Cost (1)	Technological Maturity (2)	Treatment Needed (3)	Additives Needed (4)	Market (5)	Environmental Performance (6)		Score
Importance Factor (7)	1	1	1	1	1	1	1		
Fertilizer & Soil Amendment	5	4	3	4	4	3	3		26
Cement and Concrete	3	4	4	4	4	4	5		28
Geotechnical Material	2	5	2	4	5	3	4		25
Activated Carbon, Zeolite, Adsorption Substrate	5	2	2	2	5	1	3		20
Bricks, Glass, Ceramics, Composites	1	2	1	2	3	2	4		15
Unburned Carbon Fuel	2	3	3	2	5	2	4		21
Landfill Construction	1	5	5	5	5	1	4		26
Mine Filler	2	5	3	5	5	2	4		26

All technological aspects will be ranked from 1 to 5 based upon the expected performance of a product.
1. Production cost will be estimated so that 5 will represent the lowest expected cost and 1 will be the highest expected cost.
2. Technological maturity will be estimated so that 5 will represent a fully mature technology and 1 will be a completely theoretical technology with no practical demonstration.
3. Treatment will be estimated so that 5 will represent no treatment and 1 will be for the most highly intensive treatment process.
4. Additives needed will be estimated so that 5 will represent no additives needed and 1 will require large amounts of additives.
5. Market will be estimated so that 5 will represent a large market that could utilize almost all of the BA produced and 1 will represent a small market where a small percentage of BA may be utilized.
6. Environmental performance will be estimated so that 5 will represent minimal release of harmful substances and 1 will represent exceptional release of harmful substances due to the technology chosen.
7. Importance factor may allow for one technological aspect to account for more than another

The table also allowed for elimination of some utilization options from further study in this thesis due to feasibility issues, scoring of technical aspects in the table and

the need to limit the scope of this thesis. Activated carbon or unburned carbon for fuel was not deemed feasible for further study because the amount of carbon in the subject BAs is low. Likewise, the technology for creating zeolites or other adsorption substrates is not currently mature, and the subject is beyond the scope of this thesis. Solid materials such as bricks, ceramics, glass or composites are not evaluated further due to limited technological maturity, intense processing and energy input and a potentially limited market for such products.

8 SPECIFIC AREAS OF STUDY FOR THIS THESIS

Based on the analysis of technologies detailed in Section 7 and by interest from Ekokem, a more in depth study of select BA samples from three specific locations was chosen for this thesis. Chemical and physical analyses of the whole ash samples for comparison to standards for fertilizer use, earth construction and for disposal in a landfill were chosen for initial study. Additionally, XRD analysis of the subject BAs was completed to determine the content of compounds associated with cement.

Separation was chosen for the method of refinement and a laboratory scale air classifier was chosen to complete the separations. Chemical and physical analysis of whole BA samples and separated BA samples was chosen to assess the results of separation and if separation would be a beneficial technology for meeting criteria in the above mentioned uses for BA. A more in depth description of each reuse scheme for BA is detailed in this section. Detailed descriptions of the materials used and experimental design are included in Section 9.

8.1 Forest or Agricultural Fertilizer

Assessment to determine if levels of regulated elemental constituents were in exceedance of regulatory values for agricultural or forestry use in the subject BAs. If concentrations of one or more elemental species exceeded the regulatory limit, then separation of the ash into coarse and fine fractions in order to concentrate problem elements into one fraction. This was hypothesized to produce a “clean” coarse ash fraction by concentrating heavy metals into the fine ash fraction for use as an agricultural or forestry fertilizer or soil amendment. This is based on previous studies which have demonstrated that separation technologies and air classification have been effective for concentrating components of ash into different size fractions. This has been evidenced in previous research by Camerani et al. 2002 and Pesonen 2012; however, to the knowledge of the author, research utilizing air classification for the purpose of separating problem chemical species from BA has not been done before.

8.2 Earth Construction Material

An evaluation of the chemical properties of the subject ash samples as they pertained to limit values for use in earthen construction defined by Finnish legislation. If

whole samples of the subject BAs did not meet specifications for use in earth construction then the feasibility of using air classification to meet those specifications was evaluated.

8.3 Waste Stabilization

It is expected that if the benefits of air classification were realized in lowering the concentration of heavy metals in coarse ash fractions for usage in the above proposed products, then fine ash fractions would need additional utilization or would likely need to be disposed as hazardous waste. Some of the whole BAs studied in this thesis have previously been used by Ekokem in waste stabilization. These BAs work well in this application because they contain alkaline metals that increase pH, they absorb water and they provide some hardening effect. It is hypothesized that fine fractions of fly ash should exhibit better characteristics for waste stabilization than whole ash samples. Fine ash should have higher concentrations of alkaline compounds, have a greater surface area for water absorption and possibly better hardening characteristics than unclassified BAs. Finally, this application would provide a useful service for fine fractions of BA which could be expensive to dispose.

8.4 Landfill Construction and Disposal

An evaluation of the chemical properties of the subject ash samples as they pertained to regulatory values for determination of waste status for disposal in landfill, and the suitability of the subject ashes for use in the construction of landfills. This was done as a final measure to obtain a method of ash disposal or usage if the other evaluations for ash usage are not feasible.

EXPERIMENTAL SECTION

9 MATERIALS AND METHODS

Information regarding the BAs of interest, their sources and generation, sampling of BAs, handling of BAs, experimental design, equipment used, experiments carried out, analyses and analytical methods, and any other pertinent details are outlined in this section.

9.1 BA Samples

The BAs in this thesis were chosen by Ekokem for their market potential for reuse among other undisclosed business factors.

9.1.1 Sources

The sources of BAs used in this thesis, and specific characteristics of the BAs such as fuel type, furnace type, environmental controls, etc. are detailed on a sample by sample basis in Table 7 below. Additionally, a description of each ash sample is provided along with a photo of the ash.

The aspects of the equipment and fuel used at specific production locations are summarized to best describe the most influential effects on ash formation and production. A detailed summary of ash composition, formation and the aspects that influence those was presented in Sections 3 and 3.1 of this thesis. Fuel types were mentioned in each sites' environmental permit, but were sometimes generalized, for example, wood processing waste or sawmill byproducts. The furnace type and emission systems at the plant are mentioned because they directly influence the formation and recovery of ash.

Other information that was considered but left out of the table was fuel origin and furnace temperature. Because of the constant variability of fuel origin, this aspect of ash formation and production is too acute to generalize. Likewise, furnace temperature always falls in the range of 650 to 900ºC for fluidized bed furnaces. However, temperatures in the bed, furnace and superheaters are stratified in addition to being variable due to plant conditions. Therefore, these aspects were excluded from the table since other aspects such as fuel type and percentage and furnace type are more important.

Table 7: BA source information.

Information	BA-1	BA-2	BA-3
Fuel type	Wood, peat, natural gas	wood processing waste, peat, bark, sludges, wood chips, other wastes	bark + fiber sludge, wood chips, sawmill byproducts, other biofuels, peat and oil
Furnace type	bubbling fluidized bed	bubbling fluidized bed	bubbling fluidized bed
Emission system	bag filter	ESP	ESP

BA-1

BA-1 was a brown powder with a small amount of black incompletely burned wood particles approximately 1-2 mm in size with some larger and smaller parts. After classification the coarse fraction was a dark brown fine to very fine sand like material including the black char pieces, while the fine fraction was a light brown powder that tended to agglomerate. The ash was difficult to classify because of its tendency to agglomerate in the classifier feed, and did not have consistently complete classifications compared to the other BAs.

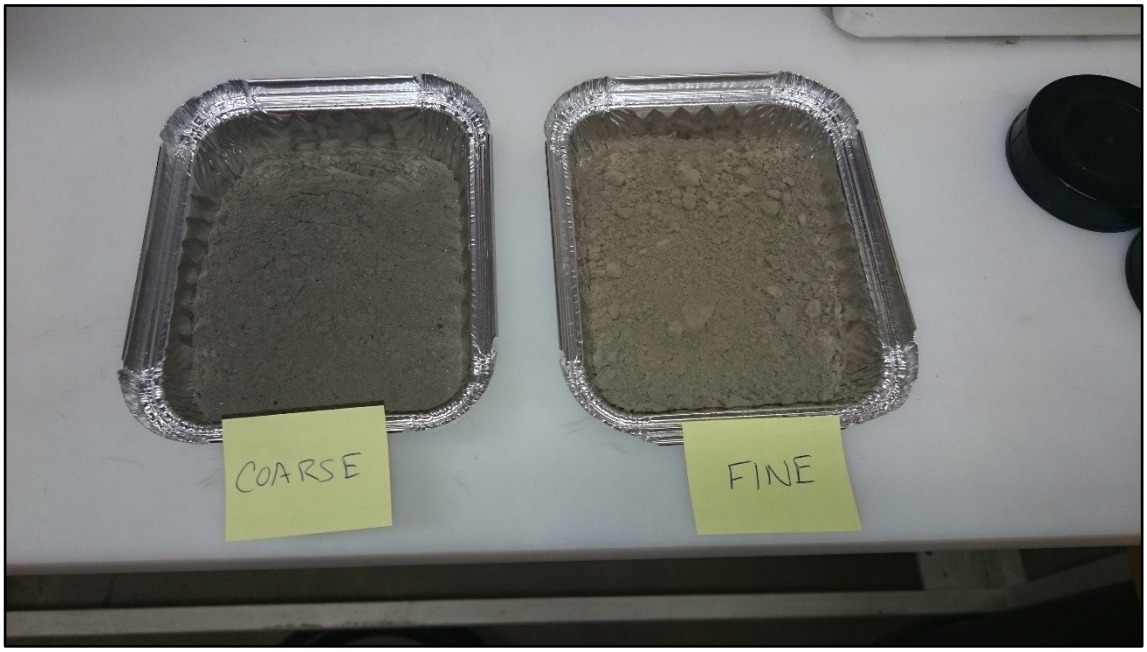

Figure 6: Air classified sample of BA-1, uncalculated mass percentages.

BA-2

BA-2 was a light brown powder, slightly coarser than BA-1. It included incompletely burned wood particles in a smaller amount than what was observed in the BA-1 samples, but similar particle sizes that overall tended to be smaller. After classification the coarse fraction was gray and like a fine to very fine sand, while the fine fraction was a light brown powder. Classification of this ash was easy with limited agglomeration in the classification equipment and good recoveries.

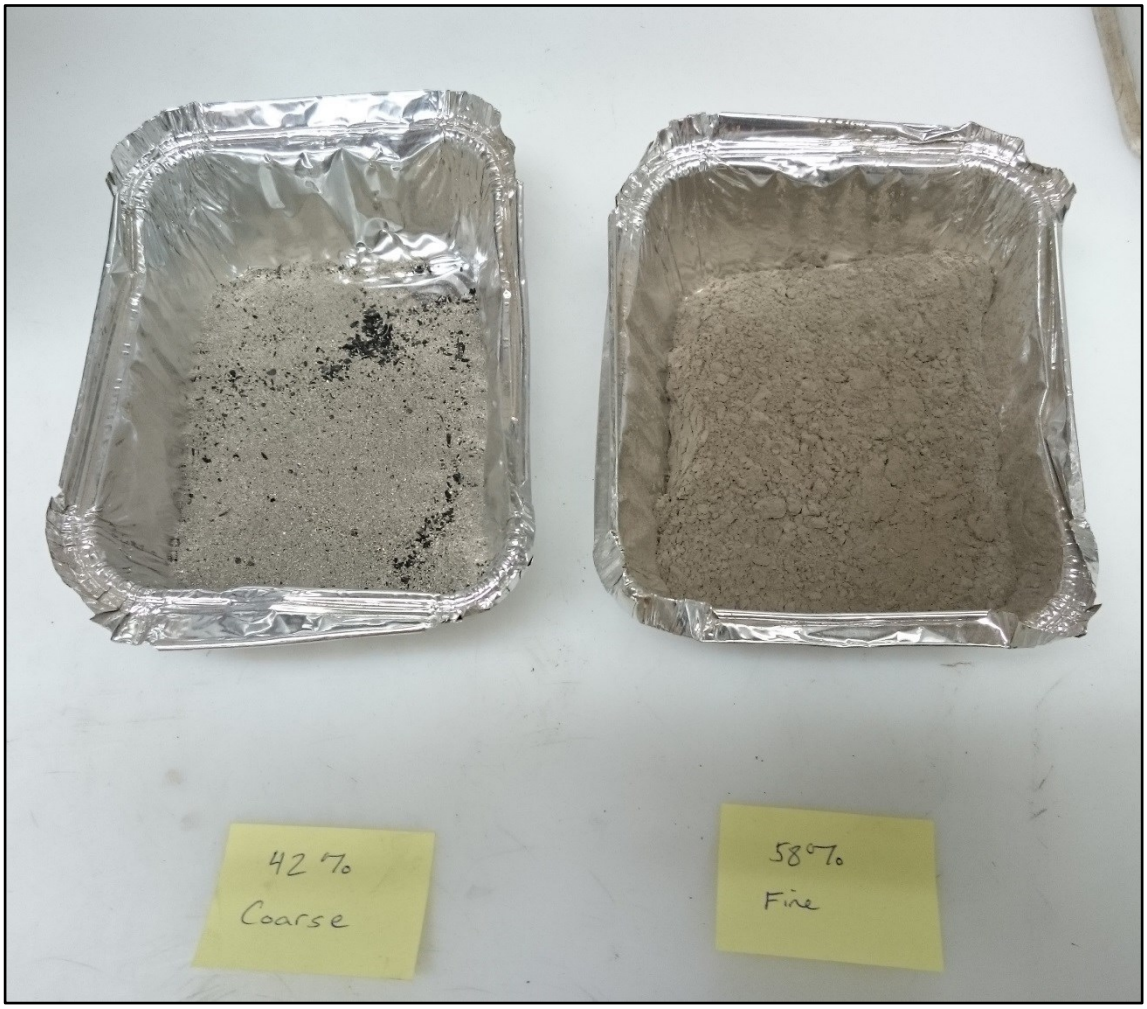

Figure 7: Air classified sample from BA-2, 42% coarse and 58% fine by mass.

BA-3

BA-3 was a light gray powder that was coarse in comparison to the other BA samples evaluated in this thesis. It had larger unburned wood pieces in the 1-3 mm range with many finer pieces of char. After classification the coarse fraction was mainly light gray, but white and black coarse particles were also observed. The coarse fraction was similar to a fine sand in consistency. The fine fraction was a light gray powder. Classification of BA-3 was very easy with consistently good recoveries and no agglomeration in the classifier feed.

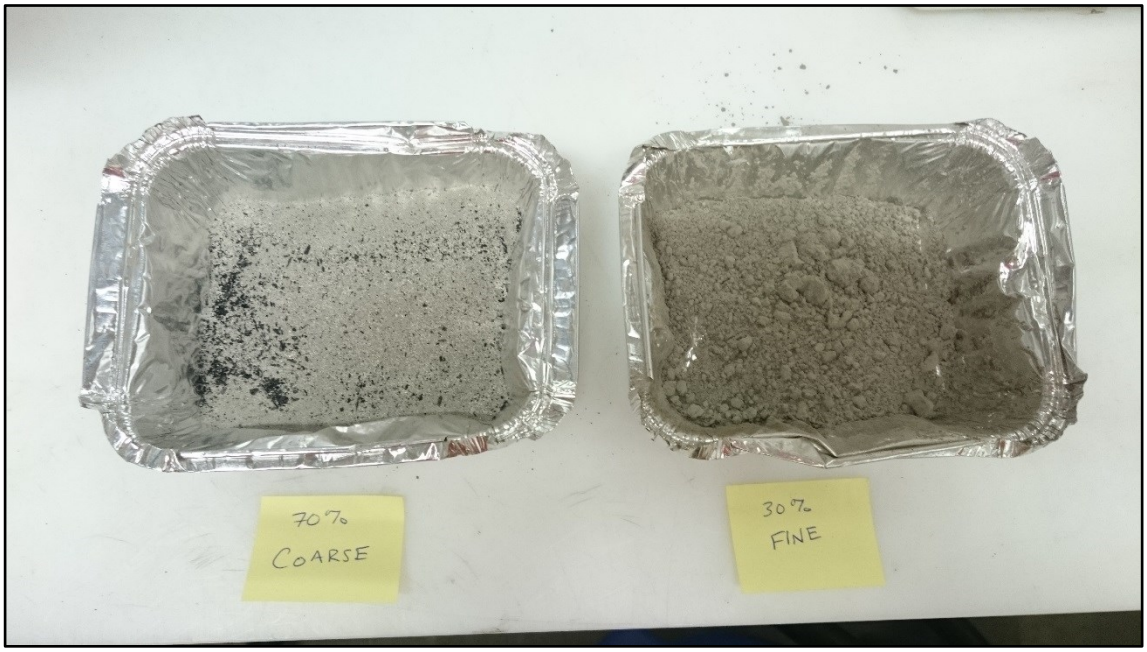

Figure 8: Air classified sample of BA-3, 70% coarse and 30% fine by mass.

9.1.2 Sample Collection

Samples were collected from the discharge point of transport vehicles used to move ash from the generator to Ekokem facilities for processing and disposal. Ash is generally expected to be thoroughly homogenized during collection and storage at the generating facility and during transfer to transport vehicles.

9.1.3 Sample Handling & Preservation

BA samples were collected in five liter plastic buckets with sealable lids. Containers were stored at room temperature in the Ekokem warehouse, which is not climate controlled. Buckets were kept sealed at all times except for extraction of sample for analysis or air classification.

9.1.4 Sample Pre-Processing

Before any separations were conducted with the air classifier, BA samples were evaluated for moisture content. Moisture content was assessed by placing ash samples of approximately 100 grams into a drying oven at 105 degrees Celsius for 2 hours. A second sample of 300 grams was placed in the same oven overnight, or approximately 20 hours. In both cases the moisture content was 0.1-0.2% which was similar to findings from previous Ekokem research. In addition, during separation a clear difference in

separation effectiveness was not noted between dried BA and BA used directly from sample buckets. Specifically, dried ash took longer to air classify because it agglomerated more in the feeding system. Therefore, it was determined that drying was not necessary because moisture content of the ash was minimal, and air classification performance was the same or better with un-dried ash.

9.2 Air Classification

Air classification was completed with a Hosokawa Alpine Multi-Plex Laboratory Classifier 100 MZR model number BA 1382/10E, and referred to as "the classifier" or "the air classifier" from this point forward. A photo of the air classifier is included below as Figure 9.

Figure 9: Hosokawa Alpine Multi-Plex Laboratory Classifier 100 MZR model number BA 1382/10E.

The air classifier allows dry powdered material such as fly ash to be separated into fractions of fine and coarse particle sizes. The difference between the fractions is defined by a particle size "cut-point", for example, if the cut-point was five micrometers

then the coarse fraction would contain all particles of sizes greater than five micrometers and the fine fraction would contain all particles of sizes smaller than five micrometers, theoretically. It is assumed from a theoretical standpoint that particles of five micrometers would be distributed evenly between the two fractions. The classifier did not have adjustments for setting the cut-point of the material being classified because each material behaves differently in the machine. Adjustments to the cut-point were made by changing the rotational speed of the classifier. In the classifier used for the described experiments, the cut-point decreases in particle size diameter as the rotational speed of the classifying mechanism was increased. Inference of the cut-point will be will be described later in this section.

The vacuum flow rate (VFR) of the air classification equipment could also be adjusted. This adjustment also influenced the classification performance of the machine and inherently the cut-point. For this study the maximum available VFR was used for each sample because it was the most efficient and consistent way to complete classification experiments. It was most efficient because higher flow rates moved the sample through the classifier quicker than lower flow rates. It should be noted that this VFR was dependent upon variables such as the classifier speed and the exhaust bag filter. It was generally noted that as the exhaust bag filter collected dust the VFR was gradually reduced. Accumulated dust was periodically loosened from the bag filter to restore VFR performance of the air classifier, and collected dust in the vacuum container was disposed as necessary.

Analysis of each ash samples' cut-points related to the percentage of ash in the coarse and fine fractions was analyzed along several different rotational speeds of the classifying mechanism. Approximately 100 grams of BA sample was classified at each stepped increase of 1000 RPM in classifier speed, through the range of possible speeds and at the maximum available VFR. This methodology was developed during initial use of the classification equipment with BA Sample 1, so results for BA-1 are slightly different from the subsequent samples.

A graph of rotations per minute versus fraction percentage is presented and for calculated cut points for each ash fraction. A regression of this graph allowed prediction of fractional yield in coarse and fine fractions according to the rotational speed of the classifying mechanism. Calculation of the cut-point diameters was performed by

inferring cut points between particle size data points in the PSD data referenced to observed fine BA percentages inferred between cumulative PSD percentages. Calculation was performed by a linear interpolation function in Excel. The basic equation is presented below; where y is the calculated cut point, x is the observed fine percentage of BA, x_1 and x_2 are cumulative percentages of BA measured in PSD analysis above and below the value of x and y_1 and y_2 are measured particle diameters corresponding to x_1 and x_2 from PSD analysis.

$$y = y_1 + (x - x_1)\frac{y_2 - y_1}{x_2 - x_1}$$

Initially, all ash samples were air classified and submitted for chemical analyses at 80% coarse and 20% fine, and 90% coarse and 10% fine fractions with the following exception. An initial sample classified from the BA-1 was classified at 81.5% coarse and 18.5% fine fractions. Later samples from all BA sources were classified to within 1% of the fractional goals. In some cases multiple air classifications were performed and the recovered coarse and fine fractions were composited for a laboratory sample. This was necessary during 90% coarse and 10% fine fractional classifications because the classification equipment could only hold approximately 500 grams of BA. With some loss of sample during classification the minimum sample mass of 50 grams required by the laboratory could not be acquired during a single classification; for example, 10% of 500 grams is 50 grams, and recovery of 100% of the 500 grams in coarse and fine fractions was not observed. Additionally, 70% coarse and 30% fine, and 65% coarse and 35% fine fractions were collected for each BA sample and held pending analysis of the 80% coarse and 20% fine, and 90% coarse and 10% fine fractions. Based on results from those samples, it was later decided that 65% coarse and 35% fine samples from BA-1 and BA-2 should be analyzed.

Data for every air classification test was recorded, including the date, time, classifier speed, VFR, total sample mass, unclassified mass, fine mass and coarse mass. Calculations of the following were also performed with the recorded data, total recovered mass (unclassified mass + coarse mass + fine mass), unrecovered mass (total

sample mass – total recovered mass), coarse % ($\frac{coarse\ mass}{coarse\ mass+fine\ mass} \times 100$) and fine % ($\frac{fine\ mass}{coarse\ mass+fine\ mass} \times 100$).

To minimize cross-contamination between the ash samples, all air classifications for each ash sample were processed in groups, for example, all air classification experiments dealing with BA-1 were performed together. Before the first air classifier experiments were done, the classifier was disassembled to the most thorough extent possible so that parts that came in contact with classified materials could be cleaned thoroughly with brushes and a vacuum. This cleaning process was also done between classifications of different BA samples. Since significant amounts of ash remained on the internal surfaces this was deemed necessary to improve quality control of classified samples submitted for analysis. Additionally, the air classifier was externally cleaned with a vacuum and brush between classifications to improve the recovery measurements of classified ash.

9.3 Physical and Chemical Analyses

Analyses completed for this project were typically performed by the laboratory at Ekokem unless otherwise specified. Available details regarding those analyses are documented in this section. PSD analysis was completed in the Aalto University laboratories utilizing laser diffraction technology with a Mastersizer 2000 analyzer made by Malvern. XRD analysis of BA samples was completed at Aalto University with a Pananalytical X'Pert ProXRD. Analysis of XRD data was performed with Match! 3 software.

10 RESULTS

The results of physical and chemical analyses as they apply to each ash sample and classified samples are summarized below.

Each whole ash sample was analyzed for PSD and the parameters required by Finnish regulations for the use of ash as fertilizer, in earth construction and for disposal in a landfill. These parameters included leaching and organic chemical analyses because there were only three samples to be analyzed. Minimization of leaching and organic analyses was preferred due to the cost and time requirements for those analyses. For the classified samples only total metal analyses and TOC were performed to determine the initial suitability of the classified ash for reuse. XRF analysis of the whole and classified BA samples was performed to identify additional elements and their destination after air classification into coarse or fine BA fractions. XRF data also indicated the presence of some micronutrients which may be interesting if the BA is utilized as an agricultural fertilizer. Finally, XRF analysis identified Cl and S concentrations in the BA samples which could be used to infer chloride and sulfate concentrations in future leaching tests.

The most useful aspect of performing PSD analyses of the BA samples in this thesis is the ability to use that data to approximate the cut point of the air classification tests that were performed. Tables produced by the Malvern Mastersizer 2000 with data used to approximate cut points are included as Appendix A.

Details regarding the air classification of all BA samples was attached in Appendix B to this thesis. This data includes the observed sample masses that were air classified and the resulting coarse, fine and unclassified masses. Calculations of the mass recoveries, fractional masses and percentages of each are presented in the data as summarized in Section 9.2.

General observations of air classification results were compiled from data collected for each sample. A summary of results describing the trends of elemental distribution after air classification was presented below as Table 8. This evaluated which elements became more concentrated in fine or coarse fractions during air classification of BA, and was based on results from total analyses by ICP and XRF analyses. A summary of all ICP and XRF data was included in Appendix C. Table 8 was organized so that if an element was observed to concentrate in all coarse or fine samples it was recorded in the columns, “All Coarse” or “All Fine.” If more than 50%

of the samples showed concentration into the coarse or fine fractions they were listed in the columns “Most Coarse” or “Most Fine.” Samples without sufficient data or those with variable results were listed as “No change or cannot be determined.” In half of the samples, Al was listed in no change or cannot be determined because those results were below detectable limits for Al. In the other half of the samples Al showed increased concentration in the coarse fraction versus the fine BA fraction. Therefore it was listed in the “Most Coarse” column in this table. Tables showing coarse and fine concentration trends from each air classification group used to create the summary Table 8 are included as Appendix D.

Table 8: Observed air classification trends for elemental distribution in study samples.

Observed Air Classification Trends for Elemental Distribution in Study Samples				
All Coarse	Most Coarse	No change or cannot be determined	Most Fine	All Fine
Zr, Si	Fe, Al	TOC, Ba, V, I, Sb, Sn, Pd, Ag, Se, Tl, Co, Ti, Mg	Ca, As, Cd, Cr, Cu, Mo, Ni, Pb, Zn,	K, P, Hg, Sr, Br, Mn, Cl, S

It should be noted that the laboratory quantitation limits (LQL) for fluoride was greater than the limit values for covered structures and paved structures; likewise, the LQL for Se was greater than the limit values for covered structures. It should be noted that the LQL for Sb, Se and fluoride were greater than the limit values for disposal in an inert waste landfill.

XRD analysis of the subject BAs was completed at Aalto University and recorded diffractograms are attached in Appendix E. Analysis of diffractograms was done with Match! 3 software and SiO_2, $CaCO_3$, CaO, MgO, Fe_2O_3, K_2O and FeO were tentatively identified in all three BA samples. It was noted that because BA is heterogeneous in particle size and in chemistry that XRD analysis and matching of compounds to diffractograms is difficult.

10.1 BA-1

PSD analysis of a whole ash sample determined that the particle sizes in BA-1 ranged between approximately 0.45 µm and 800 µm in diameter. The mean particle size was 43.87 µm in diameter; and the ash had a specific surface area of 0.507 m^2/g. The curves of cumulative and differential PSD of the BA-1 whole sample are attached as Figure 10 below.

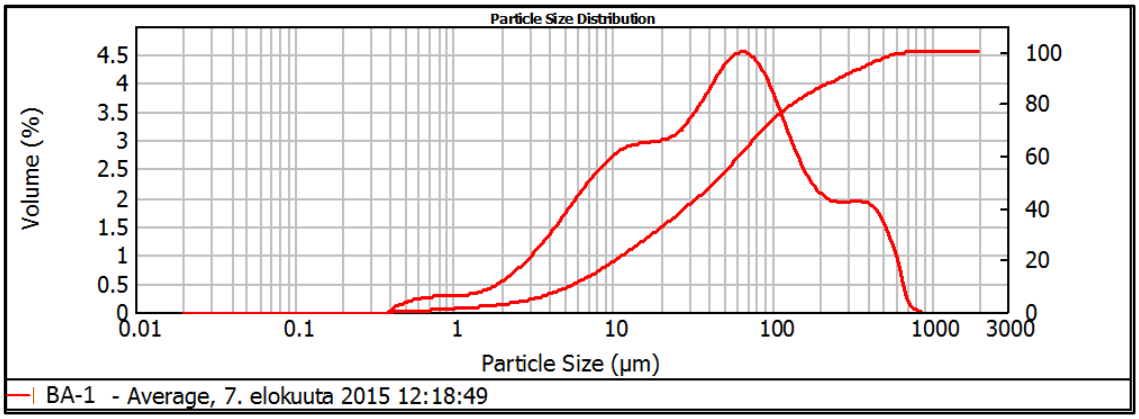

Figure 10: Cumulative and differential PSD curves for BA-1.

The relationship between the air classifier rotations per minute (RPM) and the resulting BA-1 fine percentage and associated particle size cut point is presented in Figure 11 below. The regression of the fine % vs. classifier RPM curve can be solved for RPM (x) and utilized to estimate the needed RPM for the desired fine fraction percentage (y). The equation is as follows:

$$x = -\frac{(\ln\frac{y}{103.85117})}{0.0001285}$$

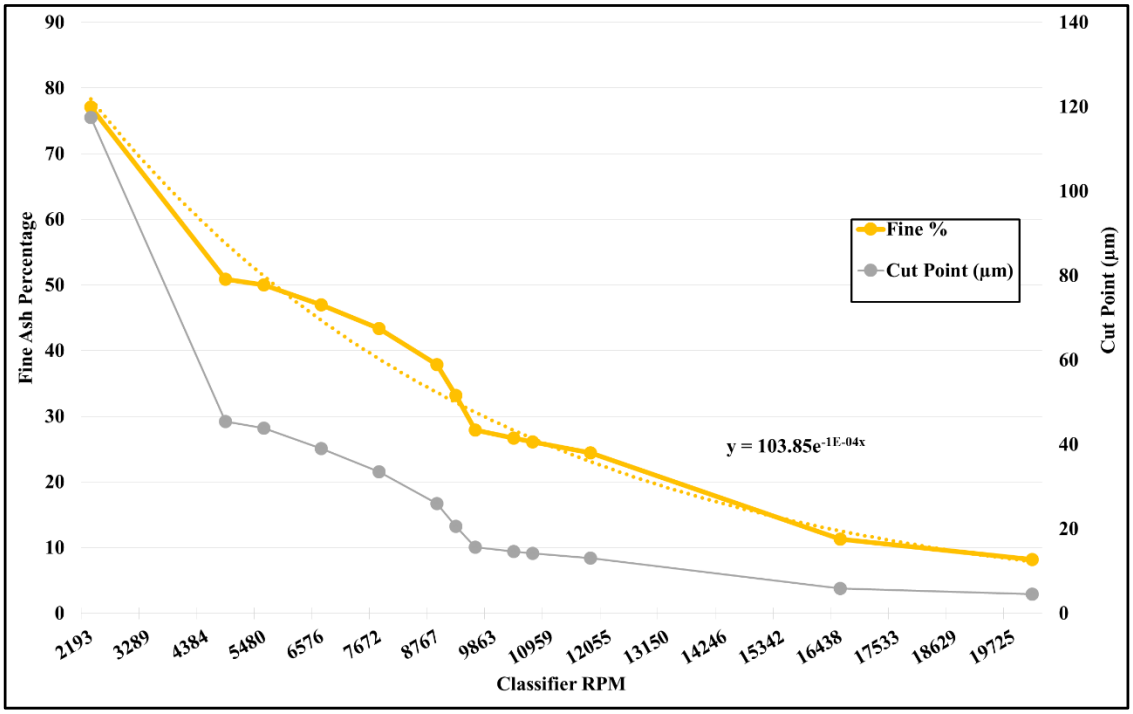

Figure 11: Graph of air classification performance for BA-1.

10.1.1 Fertilizer

Results for the evaluation of BA-1 for use as agricultural or forestry fertilizers are presented in Appendix F.

Concentrations of macronutrients Ca, P and K are displayed including P+K, because regulations for ash used as fertilizers gives limit values for Ca and P+K and not P and K individually. The limit values for these macronutrients are minimum values, so that the concentration in the ash must be greater than the limit value.

Concentrations of heavy metals in the BA-1 and air classified samples along with limit values for ash use in agricultural and forestry fertilizers are presented. Limit values for heavy metals are maximum allowable concentrations, therefore if the concentrations exceed the specific limit value the BA is not permissible for use as a fertilizer.

10.1.2 Earth Construction

Concentrations of heavy metals in BA-1 and air classified samples along with limit values for ash use in earth construction are presented in Appendix F. Limit values

for heavy metals are maximum allowable concentrations, therefore if the concentrations exceed the specific limit value the ash is not permissible for use in earth construction.

Leachate analysis was performed on BA-1 to determine suitability for use in earth construction and the results are presented in Table 9 below.

Table 9: Leachate concentrations pertaining to earth construction and limit values for use in earth construction from BA-1.

Constituent	Limit value covered structure	Limit value paved structure	BA-1
			mg/kg
DOC	500	500	<100
Antimony (Sb)	0.06	0.2	<0.50
Arsenic (As)	0.5	1.5	<0.11
Barium (Ba)	20	60	2.2
Cadmium (Cd)	0.04	0.04	<0.010
Chromium (Cr)	0.5	3.0	**6.9**
Copper (Cu)	2.0	6.0	<0.10
Mercury (Hg)	0.01	0.01	<0.0010
Lead (Pb)	0.5	1.5	**1.7**
Molybdenum (Mo)	0.5	6.0	**1.5**
Nickel (Ni)	0.4	1.2	<0.10
Vanadium (V)	2.0	3.0	<0.10
Zinc (Zn)	4.0	12	1.7
Selenium (Se)	0.1	0.5	<0.28
Fluoride (F^-)	10	50	**<100**
Sulfate (SO_4^{2-})	1000	10000	**30000**
Chloride (Cl^-)	800	2400	**3700**

BOLD indicates concentration exceeding limits for covered structures

indicates concentration exceeding limits for paved structures

10.1.3 Landfill

Leachate analysis was performed on BA-1 to determine landfill disposal eligibility and the results are presented in Table 10 below.

Table 10: Results for BA-1 landfill requirements.

Analyte	Limit values (mg/kg) of dry solid for inert waste landfill (L/S = 10 L/kg)	Limit values (mg/kg) of dry solid for non-hazardous waste landfill (L/S = 10 L/kg)	Limit values (mg/kg) of dry solid for hazardous waste landfill (L/S = 10 L/kg)	BA-1
				mg/kg
Arsenic (As)	0.5	2.0	25	<0.11
Barium (Ba)	20	100	300	2.2
Cadmium (Cd)	0.04	1.0	5.0	<0.010
Chromium (Cr)	0.5	10	70	**6.9**
Copper (Cu)	2.0	50	100	<0.020
Mercury (Hg)	0.01	0.2	2.0	<0.0010
Molybdenum (Mo)	0.5	10	30	**1.5**
Nickel (Ni)	0.4	10	40	<0.10
Lead (Pb)	0.5	10	50	**1.7**
Antimony (Sb)	0.06	0.7	5.0	**<0.50**
Selenium (Se)	0.1	0.5	7.0	**<0.28**
Zinc (Zn)	4.0	50	200	1.7
Chloride (Cl^-)	800	15000	25000	**3700**
Fluoride (F^-)	10	150	500	**<100**
Sulfate (SO_4^{2-})	1,000	20000	50000	**30000**
DOC	500	800	1000	<100
TDS	4000	60000	100000	**84000**

BOLD indicates result in excess of inert waste criteria

indicates result in excess of non-hazardous waste criteria

10.2 BA-2

PSD analysis of a whole ash sample determined that the particle sizes in the BA-2 ranged between approximately 0.45 µm and 710 µm in diameter. The mean particle size was 49.64 µm in diameter; and the ash had a specific surface area of 0.433 m^2/g. The curves of cumulative and differential PSD of BA-2 whole BA sample are attached as Figure 12 below.

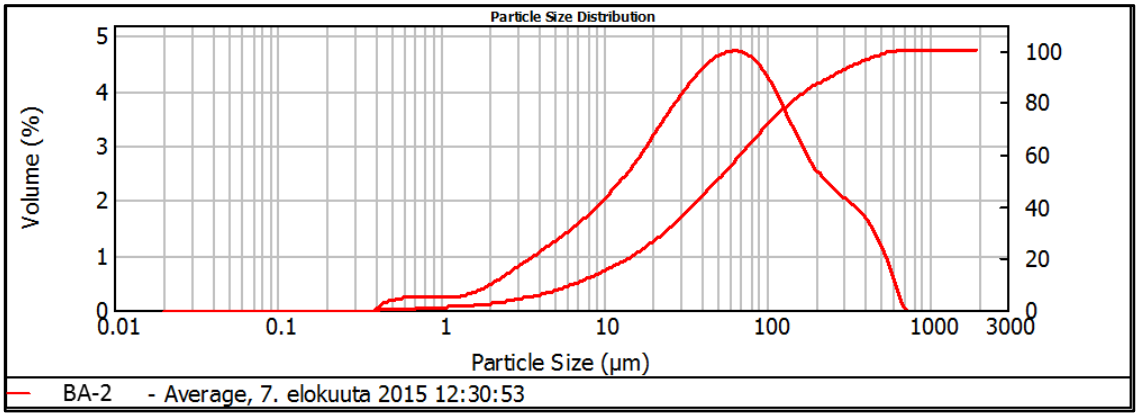

Figure 12: Cumulative and differential PSD curves for BA-2.

The relationship between the air classifier RPM and the resulting BA-2 fine percentage and associated particle size cut point is presented in Figure 13 below. The regression of the fine % vs. classifier RPM curve can be solved for RPM (x) and utilized to estimate the needed RPM for the desired fine fraction percentage (y). The equation is as follows:

$$x = -\frac{(\ln \frac{y}{113.7369041})}{0.0001397}$$

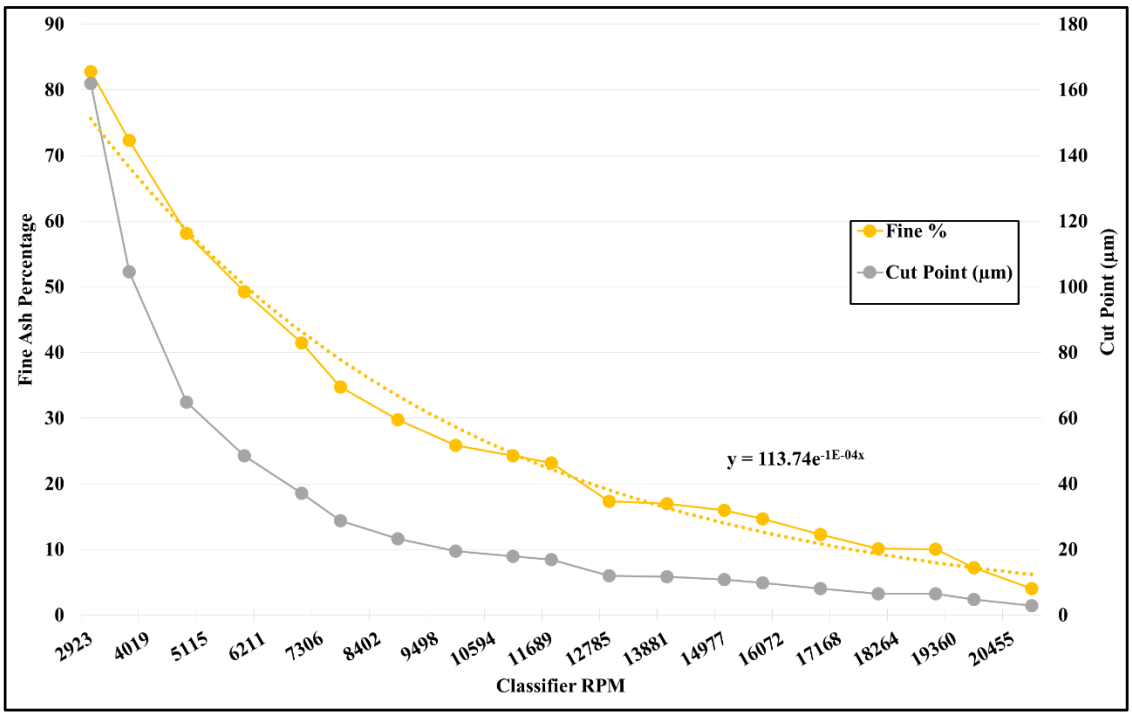

Figure 13: Graph of air classification performance for BA-2.

10.2.1 Fertilizer

Results for the evaluation of BA-2 for use as agricultural or forestry fertilizers are presented in graphical form below as Appendix F.

Concentrations of macronutrients Ca, P and K are displayed including P+K, because regulations for ash used as fertilizers gives limit values for Ca and P+K and not P and K individually. The limit values for these macronutrients are minimum values, so that the concentration in the ash must be greater than the limit value.

Concentrations of heavy metals in BA-2 and air classified samples along with limit values for ash use in agricultural and forestry fertilizers are presented. Limit values for heavy metals are maximum allowable concentrations, therefore if the concentrations exceed the specific limit value the ash is not permissible for use as a fertilizer.

10.2.2 Earth Construction

Concentrations of heavy metals in BA-2 and air classified samples along with limit values for ash use in earth construction are presented in Appendix F. Limit values for heavy metals are maximum allowable concentrations, therefore if the concentrations exceed the specific limit value the ash is not permissible for use in earth construction.

Leachate analysis was performed on BA-2 to determine suitability for use in earth construction and the results are presented in Table 11 below. This analysis was performed prior to the start of this thesis, and analysis of DOC and V were not performed.

Table 11: Leachate concentrations pertaining to earth construction and limit values for use in earth construction in BA-2.

Constituent	Limit value covered structure	Limit value paved structure	BA-2
			mg/kg
DOC	500	500	NA
Antimony (Sb)	0.06	0.2	<0.50
Arsenic (As)	0.5	1.5	<0.10
Barium (Ba)	20	60	2.5
Cadmium (Cd)	0.04	0.04	<0.010
Chromium (Cr)	0.5	3.0	**0.89**
Copper (Cu)	2.0	6.0	<0.10
Mercury (Hg)	0.01	0.01	<0.010
Lead (Pb)	0.5	1.5	<0.11
Molybdenum (Mo)	0.5	6.0	**1.2**
Nickel (Ni)	0.4	1.2	<0.10
Vanadium (V)	2.0	3.0	NA
Zinc (Zn)	4.0	12	1.2
Selenium (Se)	0.1	0.5	**<0.21**
Fluoride (F^-)	10	50	**<100**
Sulfate (SO_4^{2-})	1000	10000	**16000**
Chloride (Cl^-)	800	2400	**3200**

BOLD indicates concentration exceeding limits for covered structures

indicates concentration exceeding limits for paved structures

NA indicates that the analyte was not analyzed

10.2.3 Landfill

Leachate analysis was performed on BA-2 to determine landfill disposal eligibility and the results are presented in Table 12 below. This analysis was performed prior to the start of this thesis, and analysis of TDS was not performed.

Table 12: Results for BA-2 landfill requirements.

Analyte	Limit values (mg/kg) of dry solid for inert waste landfill (L/S = 10 L/kg)	Limit values (mg/kg) of dry solid for non-hazardous waste landfill (L/S = 10 L/kg)	Limit values (mg/kg) of dry solid for hazardous waste landfill (L/S = 10 L/kg)	BA-2
				mg/kg
Arsenic (As)	0.5	2.0	25	<0.10
Barium (Ba)	20	100	300	2.5
Cadmium (Cd)	0.04	1.0	5.0	<0.010
Chromium (Cr)	0.5	10	70	**0.89**
Copper (Cu)	2.0	50	100	<0.10
Mercury (Hg)	0.01	0.2	2.0	<0.010
Molybdenum (Mo)	0.5	10	30	**1.2**
Nickel (Ni)	0.4	10	40	<0.10
Lead (Pb)	0.5	10	50	<0.11
Antimony (Sb)	0.06	0.7	5.0	**<0.50**
Selenium (Se)	0.1	0.5	7.0	**<0.21**
Zinc (Zn)	4.0	50	200	1.2
Chloride (Cl^-)	800	15000	25000	**3200**
Fluoride (F^-)	10	150	500	**<100**
Sulfate (SO_4^{2-})	1,000	20000	50000	**16000**
DOC	500	800	1000	<100
TDS	4000	60000	100000	NA

BOLD indicates result in excess of inert waste criteria

indicates result in excess of non-hazardous waste criteria

NA indicates sample not analyzed for a specific analyte

10.3 BA-3

PSD analysis of a whole ash sample determined that the particle sizes in BA-3 ranged between approximately 0.45 μm and 800 μm in diameter. The mean particle size was 73.33 μm in diameter; and the ash had a specific surface area of 0.377 m^2/g. The curves of cumulative and differential PSD of the BA-3 whole sample are attached as Figure 14 below.

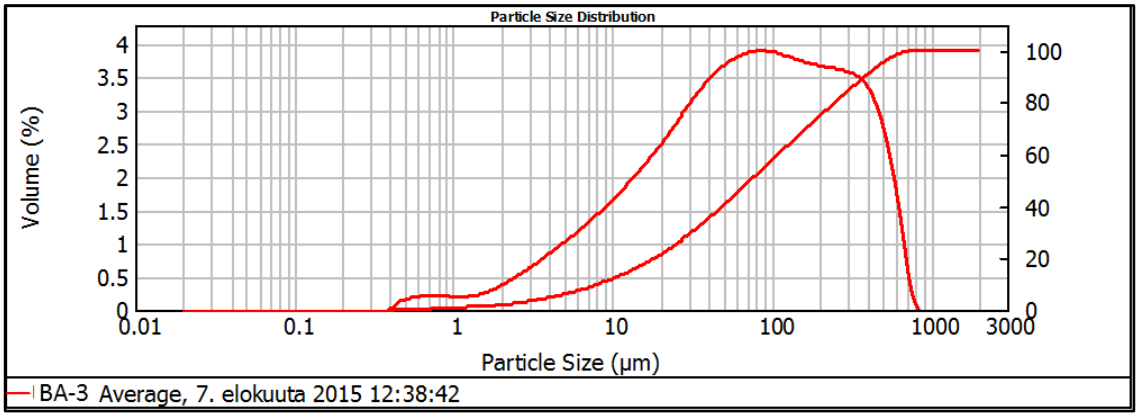

Figure 14: Cumulative and differential PSD curves for BA-3.

The relationship between the air classifier RPM and the resulting BA-3 fine percentage and associated particle size cut points is presented in Figure 15 below. The regression of the fine % vs. classifier RPM curve can be solved for RPM (x) and utilized to estimate the needed RPM for the desired fine fraction percentage (y). The equation is as follows:

$$x = -\frac{(\ln \frac{y}{85.3641152})}{0.0001427}$$

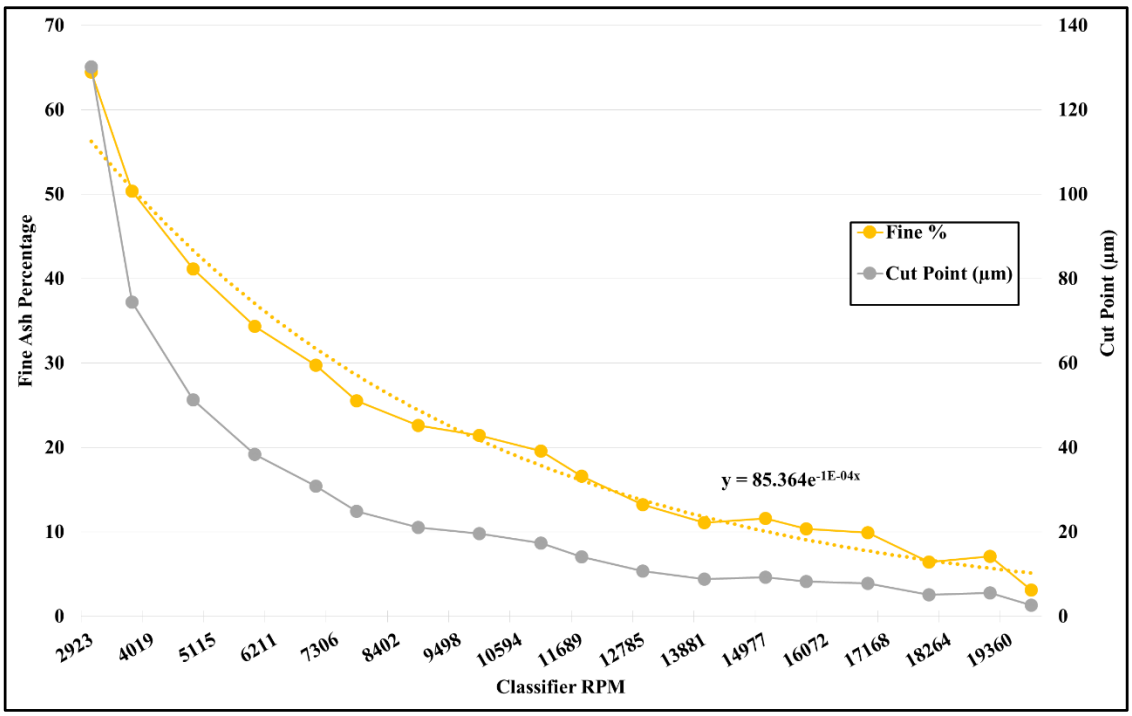

Figure 15: Graph of air classification performance for BA-3.

10.3.1 Fertilizer

Results for the evaluation of BA-3 for use as agricultural or forestry fertilizers are in Appendix F.

Concentrations of macronutrients Ca, P and K are displayed including P+K, because regulations for ash used as fertilizers gives limit values for Ca and P+K and not P and K individually. The limit values for these macronutrients are minimum values, so that the concentration in the ash must be greater than the limit value.

Concentrations of heavy metals in BA-3 and air classified samples along with limit values for ash use in agricultural and forestry fertilizers are presented. Limit values for heavy metals are maximum allowable concentrations, therefore if the concentrations exceed the specific limit value the ash is not permissible for use as a fertilizer.

10.3.2 Earth Construction

Concentrations of heavy metals in BA-3 and air classified samples along with limit values for ash use in earth construction are presented in Appendix F. Limit values for heavy metals are maximum allowable concentrations, therefore if the concentrations exceed the specific limit value the ash is not permissible for use in earth construction.

Leachate analysis was performed on BA-3 to determine suitability for use in earth construction and the results are presented in Table 13 below.

Table 13: Leachate concentrations pertaining to earth construction and limit values for use in earth construction in BA-3.

Constituent	Limit value covered structure	Limit value paved structure	BA-3
			mg/kg
DOC	500	500	<100
Antimony (Sb)	0.06	0.2	<0.50
Arsenic (As)	0.5	1.5	<0.10
Barium (Ba	20	60	**110**
Cadmium (Cd)	0.04	0.04	<0.010
Chromium (Cr)	0.5	3.0	<0.10
Copper (Cu)	2.0	6.0	<0.10
Mercury (Hg)	0.01	0.01	<0.0010
Lead (Pb)	0.5	1.5	<0.10
Molybdenum (Mo)	0.5	6.0	0.12
Nickel (Ni)	0.4	1.2	<0.10
Vanadium (V)	2.0	3.0	<0.10
Zinc (Zn)	4.0	12	0.14
Selenium (Se)	0.1	0.5	**<0.20**
Fluoride (F^-)	10	50	**<100**
Sulfate (SO_4^{2-})	1000	10000	<500
Chloride (Cl^-)	800	2400	290

BOLD indicates concentration exceeding limits for covered structures

indicates concentration exceeding limits for paved structures

10.3.3 Landfill

Leachate analysis was performed on BA-3 to determine landfill disposal eligibility and the results are presented in Table 14 below.

Table 14: Results for BA-3 landfill requirements.

Analyte	Limit values (mg/kg) of dry solid for inert waste landfill (L/S = 10 L/kg)	Limit values (mg/kg) of dry solid for non-hazardous waste landfill (L/S = 10 L/kg)	Limit values (mg/kg) of dry solid for hazardous waste landfill (L/S = 10 L/kg)	BA-3
				mg/kg
Arsenic (As)	0.5	2.0	25	<0.10
Barium (Ba)	20	100	300	**110**
Cadmium (Cd)	0.04	1.0	5.0	<0.010
Chromium (Cr)	0.5	10	70	<0.10
Copper (Cu)	2.0	50	100	<0.10
Mercury (Hg)	0.01	0.2	2.0	<0.0010
Molybdenum (Mo)	0.5	10	30	0.12
Nickel (Ni)	0.4	10	40	<0.10
Lead (Pb)	0.5	10	50	<0.10
Antimony (Sb)	0.06	0.7	5.0	**<0.50**
Selenium (Se)	0.1	0.5	7.0	**<0.20**
Zinc (Zn)	4.0	50	200	0.14
Chloride (Cl^-)	800	15000	25000	290
Fluoride (F^-)	10	150	500	**<100**
Sulfate (SO_4^{2-})	1,000	20000	50000	<500
DOC	500	800	1000	<100
TDS	4000	60000	100000	**18000**

BOLD indicates result in excess of inert waste criteria

indicates result in excess of non-hazardous waste criteria

11 DISCUSSION

The results from PSD analysis of all three BA samples appeared similar with variation in how the PSD is skewed towards larger or smaller diameter particles in a particular sample. The PSD of the BAs was constrained on the upper and lower limits by the methods of particulate capture and particulate behavior in the furnace and just downstream of the furnace. The smallest particles in all BA samples were just below one micron in diameter, and the largest particles were just below one millimeter in diameter. These results can be explained for the smallest particles due to particulate capture technology having greatly reduced ability and efficiency at capturing particulates below one micron in diameter. The largest particles close to one millimeter in diameter were likely pieces of char that were light enough to be entrained by flue gases and carried to particulate capture devices. Otherwise this upper limit of fly ash particles is defined by flue gas entrainment, where particles' surface area and mass are sufficiently large and small enough respectively to be carried upward and out of the furnace. Mineral based BA close to one millimeter in diameter and above is heavy enough that it will be captured with bottom ash, therefore not appearing in fly ash.

The relationship between the air classifier RPM and the resulting BA fraction percentages and cut-point particle diameters was performed initially to guide air classification for specific BA fraction percentages so that they could be chemically analyzed. This information gives a starting point for future air classification work done with the subject BA samples, and potentially other ashes by allowing a mathematical estimation of the resulting fractional percentage with a regression of the curve. Additionally, the estimated fractional percentage may be used to calculate an estimated cut-point based on PSD analysis of the whole ash fraction. Equations for the estimations are included in the results section for each BA sample. Details for each BA sample is presented in the following sub-sections.

Some general observations based on the graphs of classifier RPM versus fine BA percentage and cut-point can be made. The classification of all BA samples showed a rapid decrease in fine percentage and a decrease in cut-point as RPM was increased from its lowest setting to around 6,000 to 10,000 RPM where a more gradual decrease was noted. Between 10,000 RPM and the upper limit of the classifier RPM range very minimal reductions in fine percentage and cut-point were observed. In some cases in

this highest range of RPMs an increase or equal amount of fine BA than the previous classification was observed. This was likely due to BA recovery in the classifier with some portion a previous sample included with the next despite efforts to eliminate such sources of error. Notwithstanding, a generalized trend for each BA sample was observed and provided useful data for future classification experiments.

The observed trends for distribution of elemental constituents in the studied BA samples was clearly summarized in Table 8. Higher concentrations of the elements in the "All Coarse" and "All Fine" columns will always be expected to appear their respected BA fractions. Some concentration trend variability in BA samples may be observed from those elements listed in "Most Coarse" and "Most Fine", but it is more likely that those elements are observed in their respective BA fractions. Trends for all the other elements and TOC cannot be consistently determined by the results, and were expected to vary on a sample by sample basis.

As noted in the results, XRD analysis of BAs is difficult due to the heterogeneity of the material in particle size and in chemistry. An initial matching of compounds to diffractograms was completed; however, it would be pertinent to complete a more detailed and time consuming evaluation of the diffractograms. This is due to the following reasons, 1) the author has limited experience and knowledge in completion of this task, 2) the software utilized was a trial version without the best search database, 3) the process of matching compounds is considerably time consuming, 4) the potential for error is significant due to the previously mentioned items.

In the evaluation of leaching results for earth construction it was noted that the LQLs for Se and fluoride were greater than the limit values for covered structures. Additionally, the LQL for fluoride was greater than the limit value for paved structures. Therefore, those compounds may be in excess of the respective limit values regardless of those analytes not being detected in laboratory analysis. In the evaluation of BA samples' landfill status it was observed that the LQLs for Sb, Se and fluoride were above the limit values for inert waste. Therefore, those compounds may be in excess of the inert waste limit values regardless of those analytes not being detected in laboratory analysis. In all samples Sb, Se and fluoride were not detected above LQLs.

PCBs and PAHs were not detected in any of the whole BA samples. Therefore, in classified samples of these BAs no additional analyses for PAHs and PCBs were

performed for earth construction suitability. Classified samples are a product of the whole ash and the air classification process cannot produce or add PCBs or PAHs to the BA, so additional analysis was unwarranted.

Definitive evidence supporting the use of any particular BA sample in cement was not ascertained in this study, but some general data was observed for all BA samples for and against utilization of these BAs in cement.

The most supportive evidence for use of the subject BAs in cement is the presence of high percentages of Si and Ca shown in ICP-MS and XRF data. This is corroborated by tentative identification of CaO and SiO_2 by XRD analysis. Other typical components of cement such as MgO, Fe_2O_3 and K_2O were also tentatively identified by XRD analysis and supported by XRF and ICP-MS detections of K and Fe in BA samples. However, Mg was detected in a limited number of samples by XRF. Other typical components of Portland cement, Na_2O, Al_2O_3 and SO_3, were not identified in XRD data. However, Al and S were detected at levels similar to that of cement, but the chemical form those elements in which they exist in BA must be clarified. It is also suspected that the concentration of S in the BA likely exceeds what is normally present in cement. Additionally, the presence of Cl, P and heavy metals could be problematic in cement.

11.1 BA-1

Results of BA-1 samples are presented in Section 10.1. Tables comparing data to fertilizer limit values and earth construction limit values were presented in Appendix F. Leaching analysis data for earth construction and landfill status were attached as Table 9 and Table 10 respectively.

The whole sample did not pass screening for use as fertilizer in agriculture or forestry, or for earth construction due to exceedance of heavy metal concentrations over regulatory values in total elemental analyses. Agricultural use of the whole sample is limited by As, Cd, Pb and Zn exceeding regulatory values; forestry use was only affected by the As concentration which was greater than the regulatory value. It should be noted that macronutrient (Ca, P and K) concentrations all met standards for use in agriculture and forestry. The use of this whole BA is limited in earth construction by concentration of As and Zn exceeding standards.

Air classified samples showed improvements in the coarse fractions of BA versus the whole BA sample for use in fertilizers or earth construction. Coarse fractions 90% and 81.5% were similar to the whole BA sample, and showed some improvements in heavy metals concentrations versus the whole BA sample. Reductions in As, Cd and Zn in coarse samples 90% and 81.5% were noted with corresponding increases in As, Cd and Zn concentrations in fine BA samples 10% and 18.5%. Arsenic was reduced from above the limit value for forestry fertilizer and limit value for earth construction in the whole sample to below the respective limit values in the coarse 81.5% sample. Pb was reduced from above the limit value for agricultural fertilizer to below in the coarse 81.5% sample. Zn was reduced from above the limit value for earth construction to below in the coarse 81.5% sample. Therefore, the coarse 81.5% sample showed potential for use as a forestry fertilizer and in earth construction where the whole sample did not meet limit values.

Based on the results of the above mentioned air classified samples an additional air classification test was analyzed for its reuse potential. A 65% coarse fraction and associated 35% fine fraction were analyzed. The coarse fraction showed improvements over the 81.5% coarse fraction with As and Cd reduced below their respective limit values. However, Zn (1600 mg/kg) just exceeded the threshold value of 1500 mg/kg for agricultural fertilizer use. Additionally, this fraction, like the 81.5% fraction met limit values for total metals in earth construction.

The Air classified samples all exhibited significant mass increases of Ni, Cr and Mo; likely due to wear of stainless steel parts in the air classifier. A summary of percent increases based on mass balance calculations (whole sample versus sum of coarse and fine classified samples) are presented below as Table 15. These increases affected coarse sample 90% in meeting fertilizer and earth construction limit values. However, the sample was also excluded from use due to Zn and As above limit values.

Table 15: Observed increases in Cr, Ni and Mo in air classified samples from BA-1.

Increase %	Cr	Ni	Mo
90%/10%	254.8	659.0	891.3
81.5%/18.5%	122.5	238.2	147.9
65%/35%	123.9	374.2	479.2

The whole BA sample was analyzed by L/S = 10 L/kg leaching method to determine its suitability for use in earth construction. Limit values for covered structures were exceeded by Mo concentration; and limit values for paved structures was exceeded by Cr, Pb, sulfate and chloride concentrations. This BA was excluded from use in earth construction by total concentration of As, and leaching results indicated further barriers to this BA's potential for use in earth construction.

The evaluation of the whole BA sample by L/S = 10 L/kg leaching method for landfill disposal indicated that this whole ash sample did not meet the requirements for disposal as an inert waste nor non-hazardous waste. Concentrations in excess of the inert waste limit values for heavy metals Cr, Mo, Pb and inorganic ion chloride; concentrations of sulfate and TDS were in excess of non-hazardous waste limit values. It was concluded that if BA-1 was to be disposed in a landfill, it must be disposed of in a hazardous waste landfill.

11.2 BA-2

Results for BA-2 samples were presented in Section 10.2. Tables comparing data to fertilizer limit values and earth construction limit values were presented in Appendix F. Leaching analysis data for earth construction and landfill status were attached as Table 11 and Table 12 respectively.

The whole sample did not pass screening for use as fertilizer in agriculture or for earth construction due to exceedance of heavy metal concentrations over regulatory values in total elemental analyses. Agricultural use of the whole sample is limited by Cd and Zn exceeding regulatory values; the use of this ash as a fertilizer in forestry is permissible according to the analysis. It should be noted that macronutrient (Ca, P and K) concentrations all met standards for use in agriculture and forestry. The use of this whole BA is limited in earth construction by concentration of Zn exceeding the standard.

Air classified samples did show improvements in the coarse fractions of BA versus the whole BA sample for use in fertilizers or earth construction. Coarse fractions 90% and 80% were similar to the whole BA sample, and showed some improvements in heavy metals concentrations versus the whole BA sample. Reductions in As and Cd in coarse samples 90% and 80% were noted with corresponding increases in As and Cd

concentrations in fine BA samples 10% and 20%. Slight increases of Zn in coarse samples, and significant concentrating of Zn in fine fractions was observed. A slight decrease in Zn concentration would have been expected. However, the minor increase in the coarse fractions is either due to either variability in laboratory measurement or the unclassified fraction of BA was devoid of Zn (unlikely), thus producing increases in coarse and fine fractions.

Based on the results of the above mentioned air classified samples and addition air classification test was analyzed for its reuse potential. A 65% coarse fraction and associated 35% fine fraction were analyzed. The coarse fraction showed improvement over the 80% coarse fraction with Zn reduced below the respective limit value for agricultural use. However, Cd exceeded the limit value for agricultural fertilizer use. Additionally, this fraction met limit values for total metals in earth construction with the reduction of Zn below the total limit value.

Air classified samples all exhibited significant mass increases of Ni, Cr and Mo; likely due to wear of stainless steel parts in the air classifier. A summary of percent increases based on mass balance calculations (whole sample versus sum of coarse and fine classified samples) are presented below as Table 16. These increases did not affect coarse samples in meeting fertilizer or earth construction standards for total heavy metals concentrations. Ultimately, the coarse samples may still be used as forestry fertilizers.

Table 16: Observed increases in Cr, Ni and Mo in air classified samples from BA-2.

Increase %	Cr	Ni	Mo
90%/10%	178.6	174.1	218.9
80%/20%	64.5	86.6	117.6
65%/35%	-20.3	1.9	34.6

The whole BA sample was analyzed by L/S = 10 L/kg leaching method to determine its suitability for use in earth construction. Limit values for covered structures were exceeded by Cr and Mo concentrations; and limit values for paved structures was exceeded by sulfate and chloride concentrations. Consequently, the use of this BA is excluded from use in earth construction.

The evaluation of the whole BA sample by L/S = 10 L/kg leaching method for landfill disposal indicated that this whole ash sample did not meet the requirements for disposal as an inert waste. Concentrations in excess of the inert waste limit values for heavy metals Cr and Mo and for inorganic ions chloride and sulfate. This sample was not analyzed for TDS because the sample was collected previous to the start of this thesis. Additional L/S analysis to determine TDS for landfill determination (and missing analytes from earth construction determination) was not considered cost effective. It was concluded that if the BA-2 was to be disposed in a landfill, it must be disposed of in a non-hazardous landfill.

11.3 BA-3

Results for BA-3 samples were presented in Section 10.3. Tables comparing data to fertilizer limit values and earth construction limit values were presented in Appendix F. Leaching analysis data for earth construction and landfill status were attached as Table 13 and Table 14 respectively.

The whole sample did not pass screening for use as fertilizer in agriculture or forestry due to lack of P and K in total elemental analyses. Heavy metals concentrations were within regulatory parameters for use as agricultural and forestry fertilizers. If this BA is used as a fertilizer supplemental P and K must be added to meet standards. The use of this whole BA was not limited in earth construction by total analysis of heavy metals.

Air classified samples did not show significant improvements in the coarse fractions of BA versus the whole BA sample for use in fertilizers or earth construction. Coarse fractions 90% and 80% were similar to the whole BA sample, and showed some improvements in heavy metals concentrations versus the whole BA sample. Reductions in As and Cd in coarse sample 90% was noted with corresponding increases in As and Cd concentrations in fine BA sample 10%. The coarse 80% and fine 20% samples showed results contrary to those observed in other samples in this thesis. The coarse 80% sample had slightly higher heavy metal concentrations than the fine 20% sample. It is unknown why these samples behaved differently than other samples in this study. Air classified samples all exhibited significant mass increases of Ni, Cr and Mo; likely due to wear of stainless steel parts in the air classifier. A summary of percent increases

based on mass balance calculations (whole sample versus sum of coarse and fine classified samples) are presented below as Table 17. These increases in Cr and Ni affected coarse samples in meeting fertilizer or earth construction standards for total heavy metals concentrations. Therefore calculations of predicted concentrations based on whole sample mass inputs and the observed ratio of coarse to fine heavy metals concentrations were done. Calculated concentrations versus observed are presented below as Table 18. Based on the calculations coarse fractions of this BA would be within standards for all fertilizer use in which the measured Cr and Ni concentrations did not allow.

Table 17: Observed increases in Cr, Ni and Mo in air classified samples from BA-3.

Increase %	Cr	Ni	Mo
90%/10%	150.0	99.0	182.0
80%/20%	212.9	142.8	468.1

Table 18: Calculated Cr and Ni concentrations versus measured concentrations compared to limit values for fertilizer use.

Constituent	Limit value	Limit value	BA-3			
			Coarse (90%)	Fine (10%)	Coarse (80%)	Fine (20%)
Chromium (Cr)	300	300	290	**470**	**420**	240
Chromium (Cr) Calculated	300	300	113.0	183.1	131.7	75.3
Nickel (Ni)	100	150	**170**	**260**	**240**	**130**
Nickel (Ni) Calculated	100	150	83.6	**127.8**	97.2	52.7

BOLD indicates concentration exceeding limit value for agriculture

indicates concentration exceeding limit value for forestry

All concentrations reported in mg/kg

The whole BA sample was analyzed by L/S = 10 L/kg leaching method to determine its suitability for use in earth construction, and a summary of the results is attached as Table 13. The limit values for both earth construction uses were exceeded by the Ba concentration in this sample. This result is difficult to explain because the total Ba concentration in BA-3 was lower than in the other BA samples evaluated in this thesis. Likewise, the leached concentration of Ba is significantly higher than what was observed in other BA samples. A graphical representation of this phenomenon is attached as Figure 16. Consequently, the use of this BA was excluded from use in earth construction because of this Ba result. A fast leaching analysis of BA-3 was performed

to confirm these results. The fast leaching analysis resulted in a Ba concentration of 130 mg/kg. Therefore, Ba in this sample is in a more soluble state than in the other BAs studied in this thesis.

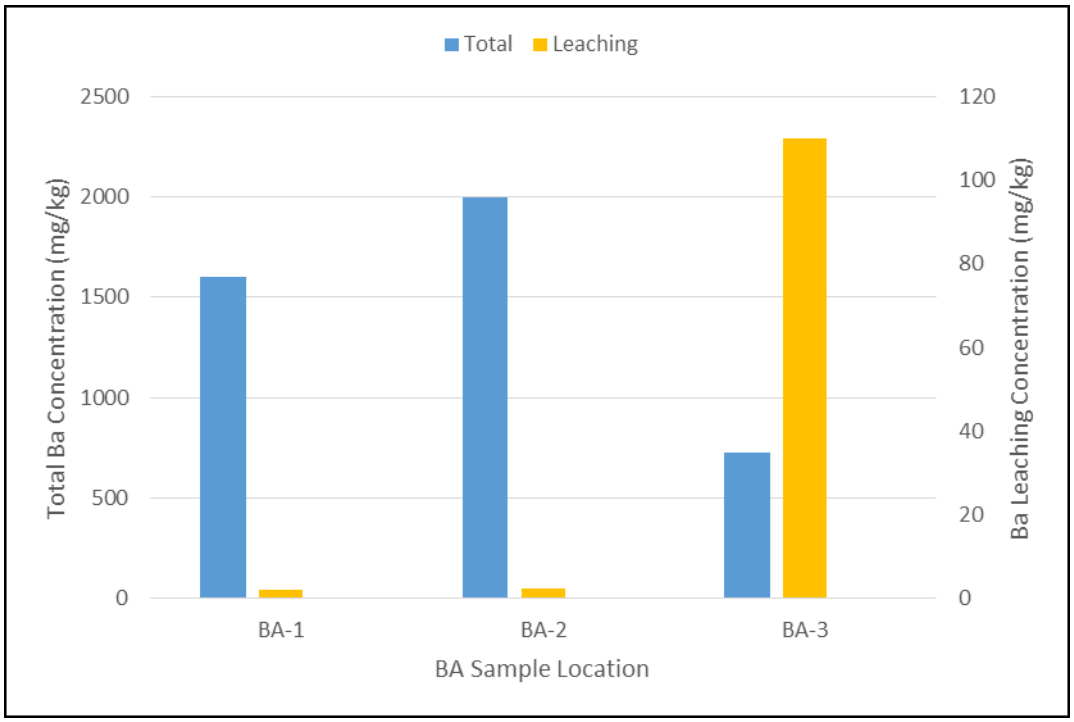

Figure 16: Total and leaching Ba concentrations in all study samples.

The evaluation of the whole BA sample by L/S = 10 L/kg leaching method for landfill disposal indicated that this whole ash sample did not meet the requirements for disposal as an inert waste nor a non-hazardous waste. The data with comparison to limit values is attached as Table 14. Concentration in excess of the inert waste and non-hazardous waste limit values for the heavy metal Ba was observed in this sample. The issue regarding Ba in this BA was discussed previously in this section. Additionally, the inert waste limit value was exceed for TDS. It was concluded that if BA-3 was to be disposed in a landfill, it must be disposed of in a hazardous waste landfill. Other BA samples exhibited higher total Ba concentrations in their BA samples, but were under the Ba limit value for inert waste. Thus, a similar result was expected for BA-3.

11.4 Potential for Error

In mass balance evaluation of certain metal species in air-classified samples compared to whole samples of ash it was noted that a significant increases were observed. It is suspected that this is a result of abrasive wear on the air classifier, specifically the stainless steel parts of the machine. Cr, Ni and Mo which are common metals in stainless steel alloys were found at elevated levels in classified samples. A summary table of affected samples and calculated percent increases of these heavy metals is included as Appendix G. This phenomenon did not greatly affect the potential for utilization of ash samples, but in some cases did contribute to the exceedance of applicable standards by the subject elements. In those cases, an estimate of the fine and coarse samples based on a mass balance calculation of the relative whole BA sample and the ratio of the corresponding element concentrations in coarse to fine BA.

Recovery of the samples added to the air classifier was closely monitored during classifier usage because it was noted that recovery of sample mass in coarse and fine fractions was not equal to the mass of the total sample that was classified. Mass loss during the classification process is due to several identified factors: ash accumulated on internal parts of the classifier, ash was lost in filtration of the vacuum system of the machine, ash adhered to the collection vessels for the input sample, coarse sample and fine sample. Therefore, recovery of samples was calculated for each classification in terms of the mass balance going into the classifier and coming out of the classifier. Also, the input samples of ash were not classified by the machine 100% in any observed classifications, and a record of the unclassified material from each classification was kept. A summary of the classifications with recovery calculations are presented in Appendix B. It was noted that the portion of unrecovered BA that was ‘lost’ to the vacuum filter was likely composed of fine ash since coarse BA was first collected in the machine and then fine BA was collected by cyclone and vacuum. Fine ash not collected by the cyclone would therefore be collected in the vacuum filter.

As discussed in Section 9.2, the air classifier was disassembled and cleaned thoroughly between the classifications of different ashes, and also cleaned externally to the best extent possible with a vacuum between classifications. This was done to minimize cross-contamination between the ash samples, thus improving the quality control of analytical samples; it was also done to improve the measurements of recovery

during air classification experiments. Despite these efforts some cross-contamination may have occurred due to ash remaining in the classifier, although there was no evidence to show that any significant cross-contamination occurred. Moreover, some recovery calculations during air classification experiments indicated recoveries over 100%, therefore recovered fractions had material in them from previous classifications. Although this was noted, it was an infrequent occurrence and not believed to be a significant source of error.

A possible source of error indicated by the classifier's operating manual was that under normal operation the mechanisms within the classifier may wear the materials that are being classified, thus changing the PSD of the whole sample by grinding larger particles into smaller particles. While important to note, no evidence was observed during this study to indicate that the ash samples under investigation experienced any significant grinding due to the air classification process.

Aging of fly ash is a significant process and was likely a contributor to error in the results of this research. There are several ways that aging of the ash in this study may have contributed to error. Since over the course of time freshly produced ash will react with moisture and CO_2 in the air, thus changing the chemical composition of the ash. In addition, this process adds mass and changes the physical characteristics, for example, the ash hardens and agglomerates into larger pieces. Therefore, precautions were enacted to limit this process. Ash samples were stored in plastic buckets that were kept sealed, and only opened for sample collection or classification. Plastic buckets were effective methods of isolation to keep the ash samples from mixing with excess air and moisture, and kept samples dry. It is reasonable to mention the mixing of ash with large amounts of air during the air classification process, but the length of time that ash samples experienced in the machine were limited to several minutes and it is not expected to have significantly aged ash samples. Inherently, avoiding BA and air contact was unavoidable in this circumstance.

12 CONCLUSIONS

First some general conclusions about air classification and analysis of BA were made and then sample specific conclusions were presented. Based on the conclusions, supplemental work to the results of this thesis are proposed.

- Future air classification experiments of BA can be guided by the methodology developed and documented in Section 9.2 of this thesis.
- Drying of the subject BAs was found to be unnecessary, and it even made air classification more difficult due to agglomeration of BA in the machine feed.
- Particle sizes of the BA (fly ash) samples have very similar range, but the distribution of particle sizes vary on a sample to sample basis. Thus, air classification performance will vary from sample to sample.
- PCBs and PAHs analysis was required for earth construction use. However, no PCBs or PAHs were not detected in any of the BA samples studied in this thesis. Therefore, no additional analyses for PCBs and PAHs was necessary in air classified samples.
- Trends for the concentrating of elemental fractions of BA with air classification were shown in Table 8 and generalized for the BA samples studied in this thesis.
- Some LQLs were greater than their respective regulatory limit values. This makes confirming the concentrations of constituents of concern difficult because they cannot technically be detected below the limit values. LQLs of concern a listed below.
    - The LQL for fluoride was greater than the limit values for covered and paved structures in earth construction.
    - The LQL for Se was greater than the limit value for covered structures in earth construction.
    - The LQLs for Sb, Se and fluoride were greater than the limit values for an inert waste landfill.
- Mass increases of Cr, Ni and Mo were noted in air classified BA samples compared to whole BA samples. This is assumed to be a result of BA wear on stainless steel parts of the air classifier. Mass balance calculations were used to

model sample concentrations without this increase for affected sample concentrations above limit values.

- Through XRD analysis, SiO_2, $CaCO_3$, CaO, MgO, Fe_2O_3, K_2O and FeO were tentatively identified in all three BA samples.
- Heterogeneity of BA makes XRD analysis difficult.
- More thorough evaluation of XRD data is needed to make more definite conclusions.
- Evidence for and against utilizing BA in cement was observed in the data from this investigation. More information is needed to make definitive conclusions for the use of the subject BA samples in cement.

BA-1

- Whole sample did not pass screening for agricultural nor forestry fertilizer, nor earth construction due to exceedance of limit values for specific heavy metal concentrations. Leaching tests also confirmed that the whole sample could not be used in earth construction.
    - Agricultural fertilizer use was limited by As, Cd, Pb and Zn.
    - Forestry fertilizer use was limited by As.
    - Earth construction use limited by total concentrations of As and Zn, and leaching tests showed Mo, Cr, Pb, sulfate and chloride limiting use.
- All problematic heavy metals and inorganic ions in this sample could theoretically be concentrated into a fine BA fraction.
- If landfilled, the whole sample must be disposed in a hazardous waste landfill because it did not pass non-hazardous limit values for Cr, Mo, Pb, chloride, sulfate and TDS.
- Air classification was used and expected to improve BA condition for reuse.
- Air classification lowered heavy metal and macronutrient concentrations in coarse fractions and increased heavy metal and macronutrient concentrations in fine fractions of BA.
- Coarse 81.5% and 65% BA showed potential for use as a forestry fertilizer and in earth construction due to separation of heavy metals by air classification.

- Zn was just above the limit value for agricultural use in the coarse 65% sample. It was the only barrier to agricultural use
- Leaching tests are needed to confirm potential use in earth construction.

BA-2

- Whole sample did not pass screening for agricultural fertilizer, nor earth construction due to exceedance of limit values for specific heavy metal concentrations. Leaching tests also confirmed that the whole sample could not be used in earth construction.
  - Agricultural fertilizer use was limited by Cd and Zn
  - Earth construction use was limited by total concentration of Zn, but leaching tests showed Cr, Mo, sulfate and chloride limiting use.
- All problematic heavy metals and inorganic ions in this sample could theoretically be concentrated into a fine BA fraction.
- If landfilled, the whole sample must be disposed in a non-hazardous waste landfill because it did not pass inert waste limit values for Cr, Mo, chloride and sulfate.
  - This sample was not analyzed for TDS.
- Air classification was used and expected to improve BA condition for reuse.
- Air classification lowered heavy metal and macronutrient concentrations in coarse fractions and increased heavy metal and macronutrient concentrations in fine fractions of BA.
- Coarse BA samples could be used as a forestry fertilizer, but there was not a significant improvement over the whole BA sample.

BA-3

- Whole sample did not pass screening for agricultural and forestry fertilizer due to lack of P+K. Heavy metals concentrations were below limit values.
  - With addition of P and/or K supplement, this BA could be used as an agricultural or forestry fertilizer.
- Earth construction limit values were not exceeded by concentrations of any total heavy metals. Use in earth construction excluded by leaching result for Ba.

- If landfilled, the whole sample must be disposed in a hazardous waste landfill because it did not pass non-hazardous waste limit value for Ba.
- The leaching result for Ba was inconsistent with other BAs in this study as noted in Section 11.3 and highlighted in Figure 16. A fast leaching test of this sample was performed and confirmed that the Ba result was correct.
- Air classification was performed to evaluate the potential for sample improvements.
- Air classification did not show significant improvements compared to the whole BA sample.
    - Increases of Cr and Ni due to air classifier wear put coarse samples over limit values for fertilizer use, and Cr made coarse 80% sample exceed limit value for earth construction.
    - These problems were resolved with mass balance calculations and coarse samples could be utilized in the same manner as the whole BA sample.
- The best solution for this BA would be to use the whole BA without air classification.

13 FUTURE WORK

Based on the results and conclusions of this thesis the following future work with these BA samples is proposed.

- A more thorough evaluation of XRD data.
- If utilization options are found for coarse fractions, then fine fractions will be considered for use as a waste stabilization media.
    - Buffering capacity and absorption capacity are proposed for testing of fine fractions.
- Sources and amounts of supplemental P and/or K for BA-3 must be determined.
- BA-3 assessed for performance of pelletizing for use as an agricultural fertilizer.
- BA-1 coarse 65% could be hardened to see if carbonation of compounds in this BA would further reduce the Zn concentration allowing use as an agricultural fertilizer.
- An evaluation of the XRF screening performance of the BAs in this thesis to support future "fast screening" of BA samples in the field or during air classification tests.
    - Comparison of XRF versus ICP data to determine accuracy of XRF data.
    - Comparison of Cl and S data from XRF analysis to chloride and sulfate results in leaching tests.

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Appendix A: PSD Tables

BA-1

Size (µm)	Vol Under %	Size (µm)		Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.020	0.00	0.142	0.00	1.002	1.30	7.096	13.83	50.238	53.69	355.656	93.64
0.022	0.00	0.159	0.00	1.125	1.52	7.962	15.62	56.368	56.98	399.052	95.09
0.025	0.00	0.178	0.00	1.262	1.74	8.934	17.53	63.246	60.36	447.744	96.48
0.028	0.00	0.200	0.00	1.416	1.98	10.024	19.54	70.963	63.77	502.377	97.76
0.032	0.00	0.224	0.00	1.589	2.25	11.247	21.64	79.621	67.13	563.677	98.81
0.036	0.00	0.252	0.00	1.783	2.56	12.619	23.79	89.337	70.36	632.456	99.59
0.040	0.00	0.283	0.00	2.000	2.93	14.159	25.99	100.237	73.39	709.627	99.93
0.045	0.00	0.317	0.00	2.244	3.37	15.887	28.20	112.468	76.18	796.214	100.00
0.050	0.00	0.356	0.00	2.518	3.88	17.825	30.43	126.191	78.69	893.367	100.00
0.056	0.00	0.399	0.00	2.825	4.49	20.000	32.67	141.589	80.93	1002.374	100.00
0.063	0.00	0.448	0.05	3.170	5.21	22.440	34.94	158.866	82.91	1124.683	100.00
0.071	0.00	0.502	0.15	3.557	6.04	25.179	37.25	178.250	84.69	1261.915	100.00
0.080	0.00	0.564	0.30	3.991	6.99	28.251	39.64	200.000	86.31	1415.892	100.00
0.089	0.00	0.632	0.48	4.477	8.07	31.698	42.13	224.404	87.83	1588.656	100.00
0.100	0.00	0.710	0.67	5.024	9.30	35.566	44.77	251.785	89.30	1782.502	100.00
0.112	0.00	0.796	0.88	5.637	10.67	39.905	47.56	282.508	90.74	2000.000	100.00
0.126	0.00	0.893	1.09	6.325	12.18	44.774	50.54	316.979	92.19		

Cumulative PSD

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	0.142	0.00	1.002	0.21	7.096	1.79	50.238	3.29	355.656	1.45
0.022	0.00	0.159	0.00	1.125	0.22	7.962	1.91	56.368	3.38	399.052	1.40
0.025	0.00	0.178	0.00	1.262	0.24	8.934	2.01	63.246	3.41	447.744	1.28
0.028	0.00	0.200	0.00	1.416	0.27	10.024	2.09	70.963	3.36	502.377	1.05
0.032	0.00	0.224	0.00	1.589	0.31	11.247	2.15	79.621	3.23	563.677	0.77
0.036	0.00	0.252	0.00	1.783	0.37	12.619	2.19	89.337	3.04	632.456	0.34
0.040	0.00	0.283	0.00	2.000	0.44	14.159	2.22	100.237	2.79	709.627	0.07
0.045	0.00	0.317	0.00	2.244	0.52	15.887	2.23	112.468	2.51	796.214	0.00
0.050	0.00	0.356	0.00	2.518	0.61	17.825	2.24	126.191	2.24	893.367	0.00
0.056	0.00	0.399	0.05	2.825	0.71	20.000	2.27	141.589	1.98	1002.374	0.00
0.063	0.00	0.448	0.10	3.170	0.83	22.440	2.31	158.866	1.78	1124.683	0.00
0.071	0.00	0.502	0.15	3.557	0.95	25.179	2.39	178.250	1.62	1261.915	0.00
0.080	0.00	0.564	0.18	3.991	1.08	28.251	2.49	200.000	1.52	1415.892	0.00
0.089	0.00	0.632	0.20	4.477	1.22	31.698	2.63	224.404	1.46	1588.656	0.00
0.100	0.00	0.710	0.21	5.024	1.37	35.566	2.80	251.785	1.44	1782.502	0.00
0.112	0.00	0.796	0.21	5.637	1.51	39.905	2.98	282.508	1.45	2000.000	
0.126	0.00	0.893	0.21	6.325	1.66	44.774	3.15	316.979	1.45		
0.142	0.00	1.002	0.21	7.096		50.238		355.656			

Differential PSD

BA-2

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.020	0.00	0.142	0.00	1.002	1.22	7.096	10.90	50.238	50.36	355.656	94.96
0.022	0.00	0.159	0.00	1.125	1.39	7.962	12.15	56.368	53.87	399.052	96.32
0.025	0.00	0.178	0.00	1.262	1.57	8.934	13.49	63.246	57.42	447.744	97.54
0.028	0.00	0.200	0.00	1.416	1.77	10.024	14.93	70.963	60.97	502.377	98.57
0.032	0.00	0.224	0.00	1.589	1.99	11.247	16.49	79.621	64.49	563.677	99.36
0.036	0.00	0.252	0.00	1.783	2.25	12.619	18.18	89.337	67.92	632.456	99.85
0.040	0.00	0.283	0.00	2.000	2.57	14.159	20.01	100.237	71.23	709.627	100.00
0.045	0.00	0.317	0.00	2.244	2.95	15.887	21.98	112.468	74.36	796.214	100.00
0.050	0.00	0.356	0.00	2.518	3.40	17.825	24.11	126.191	77.29	893.367	100.00
0.056	0.00	0.399	0.00	2.825	3.92	20.000	26.41	141.589	79.99	1002.374	100.00
0.063	0.00	0.448	0.05	3.170	4.52	22.440	28.87	158.866	82.45	1124.683	100.00
0.071	0.00	0.502	0.17	3.557	5.19	25.179	31.50	178.250	84.69	1261.915	100.00
0.080	0.00	0.564	0.32	3.991	5.95	28.251	34.29	200.000	86.73	1415.892	100.00
0.089	0.00	0.632	0.49	4.477	6.78	31.698	37.24	224.404	88.60	1588.656	100.00
0.100	0.00	0.710	0.67	5.024	7.69	35.566	40.34	251.785	90.34	1782.502	100.00
0.112	0.00	0.796	0.85	5.637	8.68	39.905	43.57	282.508	91.97	2000.000	100.00
0.126	0.00	0.893	1.04	6.325	9.75	44.774	46.92	316.979	93.51		

Cumulative PSD

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	0.142	0.00	1.002	0.18	7.096	1.24	50.238	3.51	355.656	1.36
0.022	0.00	0.159	0.00	1.125	0.18	7.962	1.34	56.368	3.55	399.052	1.22
0.025	0.00	0.178	0.00	1.262	0.20	8.934	1.44	63.246	3.55	447.744	1.03
0.028	0.00	0.200	0.00	1.416	0.22	10.024	1.56	70.963	3.51	502.377	0.79
0.032	0.00	0.224	0.00	1.589	0.26	11.247	1.69	79.621	3.43	563.677	0.50
0.036	0.00	0.252	0.00	1.783	0.32	12.619	1.83	89.337	3.31	632.456	0.15
0.040	0.00	0.283	0.00	2.000	0.38	14.159	1.97	100.237	3.14	709.627	0.00
0.045	0.00	0.317	0.00	2.244	0.45	15.887	2.13	112.468	2.93	796.214	0.00
0.050	0.00	0.356	0.00	2.518	0.52	17.825	2.30	126.191	2.70	893.367	0.00
0.056	0.00	0.399	0.05	2.825	0.60	20.000	2.46	141.589	2.46	1002.374	0.00
0.063	0.00	0.448	0.12	3.170	0.68	22.440	2.63	158.866	2.24	1124.683	0.00
0.071	0.00	0.502	0.15	3.557	0.75	25.179	2.79	178.250	2.04	1261.915	0.00
0.080	0.00	0.564	0.17	3.991	0.83	28.251	2.95	200.000	1.87	1415.892	0.00
0.089	0.00	0.632	0.18	4.477	0.91	31.698	3.10	224.404	1.74	1588.656	0.00
0.100	0.00	0.710	0.19	5.024	0.99	35.566	3.23	251.785	1.63	1782.502	0.00
0.112	0.00	0.796	0.18	5.637	1.07	39.905	3.35	282.508	1.54	2000.000	
0.126	0.00	0.893	0.18	6.325	1.15	44.774	3.44	316.979	1.45		
0.142		1.002		7.096		50.238		355.656			

Differential PSD

BA-3

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.020	0.00	0.142	0.00	1.002	1.10	7.096	9.04	50.238	40.63	355.656	88.54
0.022	0.00	0.159	0.00	1.125	1.25	7.962	10.09	56.368	43.42	399.052	91.12
0.025	0.00	0.178	0.00	1.262	1.41	8.934	11.22	63.246	46.28	447.744	93.56
0.028	0.00	0.200	0.00	1.416	1.57	10.024	12.44	70.963	49.17	502.377	95.77
0.032	0.00	0.224	0.00	1.589	1.76	11.247	13.74	79.621	52.09	563.677	97.63
0.036	0.00	0.252	0.00	1.783	1.98	12.619	15.14	89.337	55.02	632.456	99.02
0.040	0.00	0.283	0.00	2.000	2.24	14.159	16.64	100.237	57.94	709.627	99.81
0.045	0.00	0.317	0.00	2.244	2.54	15.887	18.25	112.468	60.85	796.214	100.00
0.050	0.00	0.356	0.00	2.518	2.90	17.825	19.96	126.191	63.74	893.367	100.00
0.056	0.00	0.399	0.00	2.825	3.32	20.000	21.78	141.589	66.59	1002.374	100.00
0.063	0.00	0.448	0.05	3.170	3.80	22.440	23.72	158.866	69.41	1124.683	100.00
0.071	0.00	0.502	0.16	3.557	4.35	25.179	25.79	178.250	72.21	1261.915	100.00
0.080	0.00	0.564	0.29	3.991	4.95	28.251	27.98	200.000	74.98	1415.892	100.00
0.089	0.00	0.632	0.45	4.477	5.63	31.698	30.29	224.404	77.73	1588.656	100.00
0.100	0.00	0.710	0.61	5.024	6.37	35.566	32.72	251.785	80.46	1782.502	100.00
0.112	0.00	0.796	0.78	5.637	7.19	39.905	35.26	282.508	83.18	2000.000	100.00
0.126	0.00	0.893	0.94	6.325	8.08	44.774	37.90	316.979	85.88		

Cumulative PSD

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.020	0.00	0.142	0.00	1.002	0.15	7.096	1.05	50.238	2.80	355.656	2.58
0.022	0.00	0.159	0.00	1.125	0.16	7.962	1.13	56.368	2.85	399.052	2.44
0.025	0.00	0.178	0.00	1.262	0.17	8.934	1.22	63.246	2.89	447.744	2.21
0.028	0.00	0.200	0.00	1.416	0.19	10.024	1.31	70.963	2.92	502.377	1.86
0.032	0.00	0.224	0.00	1.589	0.22	11.247	1.40	79.621	2.93	563.677	1.40
0.036	0.00	0.252	0.00	1.783	0.26	12.619	1.50	89.337	2.93	632.456	0.79
0.040	0.00	0.283	0.00	2.000	0.31	14.159	1.60	100.237	2.91	709.627	0.19
0.045	0.00	0.317	0.00	2.244	0.36	15.887	1.71	112.468	2.88	796.214	0.00
0.050	0.00	0.356	0.00	2.518	0.42	17.825	1.83	126.191	2.85	893.367	0.00
0.056	0.00	0.399	0.05	2.825	0.48	20.000	1.94	141.589	2.82	1002.374	0.00
0.063	0.00	0.448	0.11	3.170	0.54	22.440	2.07	158.866	2.79	1124.683	0.00
0.071	0.00	0.502	0.14	3.557	0.61	25.179	2.19	178.250	2.77	1261.915	0.00
0.080	0.00	0.564	0.15	3.991	0.67	28.251	2.31	200.000	2.75	1415.892	0.00
0.089	0.00	0.632	0.16	4.477	0.74	31.698	2.43	224.404	2.73	1588.656	0.00
0.100	0.00	0.710	0.17	5.024	0.82	35.566	2.54	251.785	2.72	1782.502	0.00
0.112	0.00	0.796	0.16	5.637	0.89	39.905	2.64	282.508	2.70	2000.000	
0.126	0.00	0.893	0.16	6.325	0.97	44.774	2.73	316.979	2.66		
0.142		1.002		7.096		50.238		355.656			

Differential PS

Appendix B: Air Classification Records

Sample	Date	Time	Sample	Drying Time (hr)	Drying Temp (C)	Classifier Speed (rpm)	Air Flow Rate (L/min)	Whole Sample (g)	Whole Dry Sample (g)	Whole Dry Sample (%)	Moisture (g)	Moisture (%)	Unclassified (g)	Unclassified (%)	Coarse (g)	Coarse (%)	Fine (g)	Fine (%)	Recovered [C+F] (g)	Total Recovered (g)	Total Recovered (%)	Unrecoverd (g)	Unrecoverd (%)
BA-1	24.6.2015	10:30	N	N/A	N/A	10800.0	50.0	103.2	103.2	100.0	0.0	0.0	5.1	4.9	68.2	80.0	17.1	20.0	85.3	90.4	87.6	12.8	12.4
BA-1	24.6.2015	14:30	N	2.5	105.0	10800.0	50.0	153.4	153.1	99.8	0.3	0.2	12.3	8.0	100.2	81.6	22.6	18.4	122.8	135.1	88.1	18.3	11.9
BA-1	25.6.2015	11:30	Y	20.0	105.0	10800.0	50.0	345.3	345.0	99.9	0.3	0.1	3.8	1.1	246.1	81.6	55.6	18.4	301.7	305.5	88.6	39.8	11.5
BA-1	25.6.2015	13:55	N	N/A	N/A	9800.0	52.0	102.3	102.3	100.0	0.0	0.0	13.8	13.5	60.2	66.8	29.9	33.2	90.1	103.9	101.6	-1.6	-1.6
BA-1	25.6.2015	14:10	N	N/A	N/A	8800.0	52.0	102.0	102.0	100.0	0.0	0.0	14.8	14.5	57.9	71.4	23.2	28.6	81.1	95.9	94.0	6.1	6.0
BA-1	25.6.2015	14:30	N	N/A	N/A	11800.0	48.0	101.1	101.1	100.0	0.0	0.0	5.8	5.7	68.9	88.1	9.3	11.9	78.2	84.0	83.1	17.1	16.9
BA-1	25.6.2015	15:15	N	N/A	N/A	8800.0	50.0	104.4	104.4	100.0	0.0	0.0	9.4	9.0	62.6	67.5	30.1	32.5	92.7	102.1	97.8	2.3	2.2
BA-1	25.6.2015	15:40	N	N/A	N/A	7800.0	50.0	101.8	101.8	100.0	0.0	0.0	8.3	8.2	61.5	81.1	14.3	18.9	75.8	84.1	82.6	17.7	17.4
BA-1	26.6.2015	9:10	N	N/A	N/A	8800.0	30.0	102.7	102.7	100.0	0.0	0.0	18.4	17.9	69.1	93.3	5.0	6.7	74.1	92.5	90.1	10.2	9.9
BA-1	26.6.2015	9:30	N	N/A	N/A	8800.0	61 (max)	107.2	107.2	100.0	0.0	0.0	7.9	7.4	62.0	62.1	37.8	37.9	99.8	107.7	100.5	-0.5	-0.5
BA-1	26.6.2015	9:45	N	N/A	N/A	7800.0	65 (max)	105.5	105.5	100.0	0.0	0.0	11.1	10.5	52.3	56.6	40.1	43.4	92.4	103.5	98.1	2.0	1.9
BA-1	26.6.2015	10:05	N	N/A	N/A	6800.0	65 (max)	101.6	101.6	100.0	0.0	0.0	14.1	13.9	46.4	53.0	41.1	47.0	87.5	101.6	100.0	0.0	0.0
BA-1	26.6.2015	10:15	N	N/A	N/A	5800.0	64 (max)	102.2	102.2	100.0	0.0	0.0	10.3	10.1	44.7	50.0	44.7	50.0	89.4	99.7	97.6	2.5	2.4
BA-1	26.6.2015	10:30	N	N/A	N/A	2300.0	64 (max)	103.8	103.8	100.0	0.0	0.0	4.9	4.7	22.4	22.9	75.4	77.1	97.8	102.7	98.9	1.1	1.1
BA-1	26.6.2015	10:45	N	N/A	N/A	9800.0	61 (max)	104.8	104.8	100.0	0.0	0.0	4.3	4.1	64.4	72.1	24.9	27.9	89.3	93.6	89.3	11.2	10.7
BA-1	26.6.2015	11:00	N	N/A	N/A	11800.0	60 (max)	103.8	103.8	100.0	0.0	0.0	5.7	5.5	67.7	75.6	21.9	24.4	89.6	95.3	91.8	8.5	8.2
BA-1	26.6.2015	11:15	N	N/A	N/A	20300.0	52 (max)	101.1	101.1	100.0	0.0	0.0	10.2	10.1	74.2	91.8	6.6	8.2	80.8	91.0	90.0	10.1	10.0
BA-1	26.6.2015	14:00	N	N/A	N/A	10800.0	59 (max)	101.1	101.1	100.0	0.0	0.0	6.1	6.0	64.3	73.9	22.7	26.1	87.0	93.1	92.1	8.0	7.9
BA-1	26.6.2015	14:25	N	N/A	N/A	9300.0	60 (max)	102.4	102.4	100.0	0.0	0.0	5.5	5.4	61.5	66.8	30.6	33.2	92.1	97.6	95.3	4.8	4.7
BA-1	26.6.2015	14:40	N	N/A	N/A	6000.0	59 (max)	61.5	61.5	100.0	0.0	0.0	0.6	1.0	50.3	73.3	18.3	26.7	68.6	69.2	112.5	-7.7	-12.5
BA-1	26.6.2015	14:50	N	N/A	N/A	4000.0	60 (max)	50.3	50.3	100.0	0.0	0.0	0.4	0.8	37.4	72.1	14.5	27.9	51.9	52.3	104.0	-2.0	-4.0
BA-1	26.6.2015	14:55	N	N/A	N/A	4000.0	30.0	37.4	37.4	100.0	0.0	0.0	0.4	1.1	36.8	99.5	0.2	0.5	37.0	37.4	100.0	0.0	0.0
BA-1	26.6.2015	15:00	N	N/A	N/A	3000.0	30.0	36.8	36.8	100.0	0.0	0.0	0.1	0.3	36.0	98.1	0.7	1.9	36.7	36.8	100.0	0.0	0.0
BA-1	26.6.2015	15:05	N	N/A	N/A	3000.0	60 (max)	36.0	36.0	100.0	0.0	0.0	0.4	1.1	29.5	81.7	6.6	18.3	36.1	36.5	101.4	-0.5	-1.4
BA-1	26.6.2015	15:15	N	N/A	N/A	16500.0	56 (max)	102.9	102.9	100.0	0.0	0.0	5.7	5.5	73.9	88.7	9.4	11.3	83.3	89.0	86.5	13.9	13.5
BA-1	26.6.2015	15:55	N	N/A	N/A	10300.0	56 (max)	106.0	106.0	100.0	0.0	0.0	7.4	7.0	67.1	73.3	24.5	26.7	91.6	99.0	93.4	7.0	6.6
BA-1	26.6.2015	16:10	N	N/A	N/A	5000.0	59 (max)	101.5	101.5	100.0	0.0	0.0	3.2	3.2	47.0	49.1	48.8	50.9	95.8	99.0	97.5	2.5	2.5
BA-1	20.8.2015	10:30	N	N/A	N/A	10800.0	50.0	305.3	305.3	100.0	0.0	0.0	4.8	1.6	205.7	76.4	63.7	23.6	269.4	274.2	89.8	31.1	10.2
BA-1	20.8.2015	11:30	N	N/A	N/A	10850.0	50.0	107.4	107.4	100.0	0.0	0.0	4.0	3.7	71.6	80.4	17.4	19.6	89.0	93.0	86.6	14.4	13.4
BA-1	20.8.2015	11:50	N	N/A	N/A	10860.0	50.0	206.3	206.3	100.0	0.0	0.0	4.8	2.3	140.4	76.2	43.9	23.8	184.3	189.1	91.7	17.2	8.3
BA-1	20.8.2015	13:15	Y	N/A	N/A	13800.0	55,0 (max)	106.8	106.8	100.0	0.0	0.0	6.9	6.5	73.0	80.4	17.8	19.6	90.8	97.7	91.5	9.1	8.5
BA-1	20.8.2015	13:30	Y	N/A	N/A	13800.0	54,0 (max)	208.8	208.8	100.0	0.0	0.0	6.3	3.0	147.3	81.4	33.6	18.6	180.9	187.2	89.7	21.6	10.3
BA-1	26.8.2015	10:10	N	N/A	N/A	17000.0	60 (max)	103.2	103.2	100.0	0.0	0.0	8.0	7.8	74.1	92.4	6.1	7.6	80.2	88.2	85.5	15.0	14.5
BA-1	26.8.2015	10:25	N	N/A	N/A	16000.0	50 (max)	101.8	101.8	100.0	0.0	0.0	4.7	4.6	75.4	89.2	9.1	10.8	84.5	89.2	87.6	12.6	12.4
BA-1	26.8.2015	10:40	Y	N/A	N/A	16100.0	50 (max)	507.8	507.8	100.0	0.0	0.0	4.4	0.9	399.6	87.3	58.2	12.7	457.8	462.2	91.0	45.6	9.0
BA-1	26.8.2015	11:40	Y	N/A	N/A	16500.0	50 (max)	58.2	58.2	100.0	0.0	0.0	1.0	1.7	13.0	23.0	43.6	77.0	56.6	57.6	99.0	0.6	1.0
BA-1	26.8.2015	13:05	N	N/A	N/A	11400.0	70 (max)	104.1	104.1	100.0	0.0	0.0	4.5	4.3	64.6	50.2	64.2	49.8	128.8	133.3	128.0	-29.2	-28.0
BA-1	26.8.2015	13:15	N	N/A	N/A	11400.0	70 (max)	102.8	102.8	100.0	0.0	0.0	5.0	4.9	62.0	63.3	35.9	36.7	97.9	102.9	100.1	-0.1	-0.1
BA-1	26.8.2015	13:30	Y	N/A	N/A	11500.0	70 (max)	204.7	204.7	100.0	0.0	0.0	3.9	1.9	129.0	67.1	63.3	32.9	192.3	196.2	95.8	8.5	4.2
BA-1	26.8.2015	13:50	Y	N/A	N/A	11750.0	70 (max)	63.3	63.3	100.0	0.0	0.0	3.8	6.0	1.7	3.2	51.0	96.8	52.7	56.5	89.3	6.8	10.7
BA-1	26.8.2015	14:10	Y	N/A	N/A	10750.0	70 (max)	201.0	201.0	100.0	0.0	0.0	5.9	2.9	121.1	64.3	67.1	35.7	188.2	194.1	96.6	6.9	3.4
BA-2	26.8.2015	15:00	N	N/A	N/A	3000.0	75 (max)	103.8	103.8	100.0	0.0	0.0	8.4	8.1	15.5	17.2	74.7	82.8	90.2	98.6	95.0	5.2	5.0
BA-2	26.8.2015	15:10	N	N/A	N/A	4000.0	73 (max)	106.7	106.7	100.0	0.0	0.0	4.2	3.9	27.8	27.7	72.7	72.3	100.5	104.7	98.1	2.0	1.9
BA-2	26.8.2015	15:20	N	N/A	N/A	5000.0	71 (max)	101.5	101.5	100.0	0.0	0.0	1.4	1.4	41.1	41.9	57.1	58.1	98.2	99.6	98.1	1.9	1.9
BA-2	26.8.2015	15:30	N	N/A	N/A	6000.0	71 (max)	104.1	104.1	100.0	0.0	0.0	5.3	5.1	49.0	50.7	47.6	49.3	96.6	101.9	97.9	2.2	2.1
BA-2	26.8.2015	15:40	N	N/A	N/A	7000.0	70 (max)	105.3	105.3	100.0	0.0	0.0	1.9	1.8	59.0	58.5	41.8	41.5	100.8	102.7	97.5	2.6	2.5
BA-2	26.8.2015	15:50	N	N/A	N/A	8000.0	70 (max)	106.1	106.1	100.0	0.0	0.0	3.2	3.0	64.4	65.2	34.3	34.8	98.7	101.9	96.0	4.2	4.0
BA-2	27.8.2015	9:15	N	N/A	N/A	9000.0	71 (max)	101.0	101.0	100.0	0.0	0.0	1.1	1.1	67.1	70.3	28.4	29.7	95.5	96.6	95.6	4.4	4.4
BA-2	27.8.2015	9:25	N	N/A	N/A	10000.0	70 (max)	106.3	106.3	100.0	0.0	0.0	1.0	0.9	73.7	74.1	25.7	25.9	99.4	100.4	94.4	5.9	5.6
BA-2	27.8.2015	9:35	N	N/A	N/A	11000.0	68 (max)	102.1	102.1	100.0	0.0	0.0	1.8	1.8	71.2	75.7	22.8	24.3	94.0	95.8	93.8	6.3	6.2
BA-2	27.8.2015	9:45	N	N/A	N/A	12000.0	68 (max)	104.4	104.4	100.0	0.0	0.0	2.7	2.6	72.6	76.8	21.9	23.2	94.5	97.2	93.1	7.2	6.9
BA-2	27.8.2015	9:55	N	N/A	N/A	13000.0	65 (max)	102.3	102.3	100.0	0.0	0.0	1.0	1.0	76.1	82.6	16.0	17.4	92.1	93.1	91.0	9.2	9.0

Sample	Date	Time	Sample	Drying Time (hr)	Drying Temp (C)	Classifier Speed (rpm)	Air Flow Rate (L/min)	Whole Sample (g)	Whole Dry Sample (g)	Whole Dry Sample (%)	Moisture (g)	Moisture (%)	Unclassified (g)	Unclassified (%)	Coarse (g)	Coarse (%)	Fine (g)	Fine (%)	Recovered [C+F] (g)	Total Recovered (g)	Total Recovered (%)	Unrecoverd (g)	Unrecoverd (%)
BA-2	27.8.2015	10:05	N	N/A	N/A	14000.0	65 (max)	104.7	104.7	100.0	0.0	0.0	2.7	2.6	77.2	83.0	15.8	17.0	93.0	95.7	91.4	9.0	8.6
BA-2	27.8.2015	10:15	N	N/A	N/A	15000.0	64 (max)	101.4	101.4	100.0	0.0	0.0	1.0	1.0	77.8	84.0	14.8	16.0	92.6	93.6	92.3	7.8	7.7
BA-2	27.8.2015	10:25	N	N/A	N/A	16000.0	62 (max)	101.8	101.8	100.0	0.0	0.0	4.6	4.5	75.7	85.3	13.0	14.7	88.7	93.3	91.7	8.5	8.3
BA-2	27.8.2015	10:35	N	N/A	N/A	17000.0	60 (max)	104.6	104.6	100.0	0.0	0.0	3.8	3.6	80.8	87.7	11.3	12.3	92.1	95.9	91.7	8.7	8.3
BA-2	27.8.2015	10:45	N	N/A	N/A	18000.0	59 (max)	106.2	106.2	100.0	0.0	0.0	0.8	0.8	85.5	89.9	9.6	10.1	95.1	95.9	90.3	10.3	9.7
BA-2	27.8.2015	10:55	N	N/A	N/A	19000.0	58 (max)	104.7	104.7	100.0	0.0	0.0	3.0	2.9	82.4	90.0	9.2	10.0	91.6	94.6	90.4	10.1	9.6
BA-2	27.8.2015	11:05	N	N/A	N/A	20000.0	55 (max)	104.4	104.4	100.0	0.0	0.0	2.7	2.6	87.5	92.8	6.8	7.2	94.3	97.0	92.9	7.4	7.1
BA-2	27.8.2015	11:15	N	N/A	N/A	21000.0	54 (max)	101.3	101.3	100.0	0.0	0.0	1.4	1.4	84.5	95.9	3.6	4.1	88.1	89.5	88.4	11.8	11.6
BA-2	27.8.2015	13:45	N	N/A	N/A	18500.0	64 (max)	607.3	607.3	100.0	0.0	0.0	4.7	0.8	500.4	86.5	78.3	13.5	578.7	583.4	96.1	23.9	3.9
BA-2	27.8.2015	14:15	N	N/A	N/A	19200.0	58 (max)	78.3	78.3	100.0	0.0	0.0	6.0	7.7	15.5	32.6	32.0	67.4	47.5	53.5	68.3	24.8	31.7
BA-2	27.8.2015	15:00	Y	N/A	N/A	18750.0	56 (max)	102.9	102.9	100.0	0.0	0.0	1.1	1.1	84.4	89.7	9.7	10.3	94.1	95.2	92.5	7.7	7.5
BA-2	27.8.2015	15:15	Y	N/A	N/A	18750.0	56 (max)	112.9	112.9	100.0	0.0	0.0	5.5	4.9	85.1	90.9	8.5	9.1	93.6	99.1	87.8	13.8	12.2
BA-2	27.8.2015	15:25	Y	N/A	N/A	18800.0	55 (max)	102.3	102.3	100.0	0.0	0.0	2.8	2.7	86.6	89.4	10.3	10.6	96.9	99.7	97.5	2.6	2.5
BA-2	27.8.2015	15:35	Y	N/A	N/A	19000.0	55 (max)	109.8	109.8	100.0	0.0	0.0	8.6	7.8	87.1	90.2	9.5	9.8	96.6	105.2	95.8	4.6	4.2
BA-2	27.8.2015	15:45	Y	N/A	N/A	19000.0	55 (max)	110.3	110.3	100.0	0.0	0.0	6.0	5.4	85.4	89.9	9.6	10.1	95.0	101.0	91.6	9.3	8.4
BA-2	27.8.2015	15:50	N	N/A	N/A	12500.0	60 (max)	250.0	250.0	100.0	0.0	0.0	4.7	1.9	190.3	71.7	75.2	28.3	265.5	270.2	108.1	-20.2	-8.1
BA-2	27.8.2015	16:00	Y	N/A	N/A	13500.0	60 (max)	247.1	247.1	100.0	0.0	0.0	2.3	0.9	188.9	79.6	48.5	20.4	237.4	239.7	97.0	7.4	3.0
BA-2	31.8.2015	10:10	N	N/A	N/A	8750.0	70 (max)	208.7	208.7	100.0	0.0	0.0	1.1	0.5	138.7	63.9	78.4	36.1	217.1	218.2	104.6	-9.5	-4.6
BA-2	31.8.2015	10:25	Y	N/A	N/A	9000.0	69 (max)	203.9	203.9	100.0	0.0	0.0	2.1	1.0	136.6	69.7	59.5	30.3	196.1	198.2	97.2	5.7	2.8
BA-2	31.8.2015	10:45	N	N/A	N/A	8000.0	69 (max)	205.9	205.9	100.0	0.0	0.0	2.1	1.0	132.8	66.9	65.6	33.1	198.4	200.5	97.4	5.4	2.6
BA-2	31.8.2015	11:00	N	N/A	N/A	7750.0	68 (max)	203.2	203.2	100.0	0.0	0.0	2.2	1.1	128.0	66.3	65.1	33.7	193.1	195.3	96.1	7.9	3.9
BA-2	31.8.2015	11:15	Y	N/A	N/A	7250.0	68 (max)	210.5	210.5	100.0	0.0	0.0	7.9	3.8	125.7	64.0	70.6	36.0	196.3	204.2	97.0	6.3	3.0
BA-3	31.8.2015	12:25	N	N/A	N/A	3000.0	70 (max)	101.7	101.7	100.0	0.0	0.0	0.8	0.8	35.1	35.5	63.7	64.5	98.8	99.6	97.9	2.1	2.1
BA-3	31.8.2015	12:35	N	N/A	N/A	4000.0	69 (max)	104.3	104.3	100.0	0.0	0.0	0.8	0.8	50.8	49.7	51.5	50.3	102.3	103.1	98.8	1.2	1.2
BA-3	31.8.2015	12:40	N	N/A	N/A	5000.0	68 (max)	104.6	104.6	100.0	0.0	0.0	1.1	1.1	59.4	58.9	41.5	41.1	100.9	102.0	97.5	2.6	2.5
BA-3	31.8.2015	12:50	N	N/A	N/A	6000.0	66 (max)	108.9	108.9	100.0	0.0	0.0	1.0	0.9	69.9	65.6	36.6	34.4	106.5	107.5	98.7	1.4	1.3
BA-3	31.8.2015	12:55	N	N/A	N/A	7000.0	66 (max)	105.0	105.0	100.0	0.0	0.0	0.7	0.7	71.6	70.3	30.3	29.7	101.9	102.6	97.7	2.4	2.3
BA-3	31.8.2015	13:15	N	N/A	N/A	8000.0	65 (max)	109.3	109.3	100.0	0.0	0.0	1.1	1.0	78.8	74.5	27.0	25.5	105.8	106.9	97.8	2.4	2.2
BA-3	31.8.2015	13:25	N	N/A	N/A	9000.0	65 (max)	103.0	103.0	100.0	0.0	0.0	1.1	1.1	77.4	77.4	22.6	22.6	100.0	101.1	98.2	1.9	1.8
BA-3	31.8.2015	13:35	N	N/A	N/A	10000.0	65 (max)	109.4	109.4	100.0	0.0	0.0	1.1	1.0	82.6	78.6	22.5	21.4	105.1	106.2	97.1	3.2	2.9
BA-3	31.8.2015	13:40	N	N/A	N/A	11000.0	64 (max)	110.0	110.0	100.0	0.0	0.0	1.3	1.2	84.6	80.4	20.6	19.6	105.2	106.5	96.8	3.5	3.2
BA-3	31.8.2015	13:50	N	N/A	N/A	12000.0	63 (max)	106.9	106.9	100.0	0.0	0.0	1.1	1.0	84.3	83.4	16.8	16.6	101.1	102.2	95.6	4.7	4.4
BA-3	31.8.2015	14:00	N	N/A	N/A	13000.0	61 (max)	105.6	105.6	100.0	0.0	0.0	1.2	1.1	85.3	86.8	13.0	13.2	98.3	99.5	94.2	6.1	5.8
BA-3	31.8.2015	14:05	N	N/A	N/A	14000.0	61 (max)	108.0	108.0	100.0	0.0	0.0	1.2	1.1	89.0	88.9	11.1	11.1	100.1	101.3	93.8	6.7	6.2
BA-3	31.8.2015	14:10	N	N/A	N/A	15000.0	60 (max)	106.6	106.6	100.0	0.0	0.0	1.0	0.9	89.4	88.4	11.7	11.6	101.1	102.1	95.8	4.5	4.2
BA-3	31.8.2015	14:20	N	N/A	N/A	16000.0	59 (max)	104.6	104.6	100.0	0.0	0.0	1.3	1.2	88.0	89.6	10.2	10.4	98.2	99.5	95.1	5.1	4.9
BA-3	31.8.2015	14:30	N	N/A	N/A	17000.0	58 (max)	110.0	110.0	100.0	0.0	0.0	0.8	0.7	92.6	90.1	10.2	9.9	102.8	103.6	94.2	6.4	5.8
BA-3	31.8.2015	14:40	N	N/A	N/A	18000.0	57 (max)	114.0	114.0	100.0	0.0	0.0	1.9	1.7	96.3	93.6	6.6	6.4	102.9	104.8	91.9	9.2	8.1
BA-3	31.8.2015	14:45	N	N/A	N/A	19000.0	57 (max)	106.9	106.9	100.0	0.0	0.0	3.5	3.3	89.2	92.9	6.8	7.1	96.0	99.5	93.1	7.4	6.9
BA-3	31.8.2015	14:50	N	N/A	N/A	20000.0	54 (max)	101.1	101.1	100.0	0.0	0.0	1.2	1.2	90.6	96.9	2.9	3.1	93.5	94.7	93.7	6.4	6.3
BA-3	1.9.2015	11:15	N	N/A	N/A	17000.0	60 (max)	251.7	251.7	100.0	0.0	0.0	1.0	0.4	215.7	88.1	29.2	11.9	244.9	245.9	97.7	5.8	2.3
BA-3	1.9.2015	11:30	Y	N/A	N/A	17500.0	59 (max)	250.4	250.4	100.0	0.0	0.0	0.9	0.4	215.7	90.2	23.5	9.8	239.2	240.1	95.9	10.3	4.1
BA-3	1.9.2015	11:45	Y	N/A	N/A	17400.0	57 (max)	304.9	304.9	100.0	0.0	0.0	2.2	0.7	262.5	89.8	29.8	10.2	292.3	294.5	96.6	10.4	3.4
BA-3	1.9.2015	12:10	N	N/A	N/A	11000.0	64 (max)	255.5	255.5	100.0	0.0	0.0	1.0	0.4	198.9	77.7	57.1	22.3	256.0	257.0	100.6	-1.5	-0.6
BA-3	1.9.2015	12:25	N	N/A	N/A	11100.0	64 (max)	258.5	258.5	100.0	0.0	0.0	0.8	0.3	202.2	81.1	47.0	18.9	249.2	250.0	96.7	8.5	3.3
BA-3	1.9.2015	12:40	N	N/A	N/A	10900.0	62 (max)	271.9	271.9	100.0	0.0	0.0	1.0	0.4	215.9	82.7	45.2	17.3	261.1	262.1	96.4	9.8	3.6
BA-3	1.9.2015	12:50	N	N/A	N/A	10500.0	62 (max)	272.5	272.5	100.0	0.0	0.0	1.4	0.5	220.0	83.6	43.2	16.4	263.2	264.6	97.1	7.9	2.9
BA-3	1.9.2015	13:00	N	N/A	N/A	10400.0	61 (max)	268.6	268.6	100.0	0.0	0.0	1.3	0.5	209.9	81.1	49.0	18.9	258.9	260.2	96.9	8.4	3.1
BA-3	1.9.2015	13:15	Y	N/A	N/A	10000.0	61 (max)	269.0	269.0	100.0	0.0	0.0	1.7	0.6	207.4	79.3	54.3	20.7	261.7	263.4	97.9	5.6	2.1
BA-3	1.9.2015	13:55	N	N/A	N/A	7000.0	64 (max)	202.7	202.7	100.0	0.0	0.0	1.0	0.5	143.0	71.2	57.8	28.8	200.8	201.8	99.6	0.9	0.4
BA-3	1.9.2015	14:10	Y	N/A	N/A	6750.0	62 (max)	209.8	209.8	100.0	0.0	0.0	0.6	0.3	144.8	70.5	60.6	29.5	205.4	206.0	98.2	3.8	1.8
BA-3	1.9.2015	14:25	Y	N/A	N/A	5750.0	63 (max)	192.8	192.8	100.0	0.0	0.0	1.1	0.6	124.7	65.7	65.1	34.3	189.8	190.9	99.0	1.9	1.0

Appendix C: TOC, ICP and XRF Data

Sample Location	Units	BA-1	BA-1	BA-1	BA-1	BA-1	BA-1	BA-1	BA-2	BA-2	BA-2
BA Fraction		Whole	Coarse (90%)	Fine (10%)	Coarse (81.5%)	Fine (18.5%)	Coarse (65%)	Fine (35%)	Whole	Coarse (90%)	Fine (10%)
Sample ID Number		15KK01034	15KK01740	15KK01741	15KK01147	15KK01148	15KK01853	15KK01852	15KK01174	15KK01546	15KK01543
TOC	%	0.92	<0.50	<0.50	0.72	0.51	NA	NA	0.85	0.88	<0.50
Ca	mg/kg	130000	140000	250000	110000	210000	110000	250000	200000	200000	140000
K	mg/kg	33000	35000	69000	27000	53000	35000	63000	36000	34000	49000
P	mg/kg	13000	12000	22000	10000	24000	8200	22000	17000	15000	24000
As	mg/kg	62	49	140	36	140	24	120	3.6	<5.1	6
Ba	mg/kg	1600	230	130	1400	2600	1200	1200	2000	1500	140
Cd	mg/kg	5.7	3.9	15	2.8	15	1.9	12	6.6	5.5	18
Cr	mg/kg	110	400	630	220	460	170	410	55	150	310
Cu	mg/kg	150	150	220	140	250	150	240	76	82	140
Hg	mg/kg	0.13	<0.10	0.24	<0.10	0.33	<0.10	0.38	<0.10	<0.10	0.29
Mo	mg/kg	2.8	28	55	9.9	31	10	30	3.8	11	33
Ni	mg/kg	28	220	360	85	190	90	230	34	91	190
Pb	mg/kg	130	89	240	77	260	64	220	19	20	45
V	mg/kg	35	29	28	35	39	28	33	29	28	20
Zn	mg/kg	2500	2200	4800	1800	4500	1600	4400	2200	2600	7700
XRF											
I	mg/kg	<7.7	<13	<15	<7.5	<8.6	<10	<13	<12	<12	<14
Sb	mg/kg	<29	<39	<46	<28	<32	<34	<39	<38	<36	<41
Sn	mg/kg	<26	<40	<45	<25	<28	<34	<40	<37	<37	<41
Pd	mg/kg	<8.0	<5.6	<6.7	<7.8	<9.1	<4.6	<5.9	<5.2	36	92
Ag	mg/kg	<12	<100	<59	<12	<15	<58	<60	<110	<110	<98
Zr	mg/kg	110	110	12	100	21	140	32	270	280	130
Sr	mg/kg	560	470	770	460	810	400	770	450	420	620
Br	mg/kg	16	14	40	14	39	12	32	93	52	260
Se	mg/kg	<3.9	<3.7	<5.9	<3.9	<4.7	<3.1	<5.0	<4.3	<3.4	<4.8
Tl	mg/kg	<10	<12	<18	<9.2	<13	<9.6	<14	<10	<9.3	<13
Co	mg/kg	<100	<140	<130	<110	<110	<110	<120	<120	<120	<110
Fe	mg/kg	15000	16000	13000	17000	13000	17000	15000	16000	18000	13000
Mn	mg/kg	9200	6500	12000	7100	14000	5600	13000	12000	11000	18000
Ti	mg/kg	4400	3500	4300	4800	4200	4400	5300	3600	3900	2800
Al	mg/kg	23000	<2700	<4400	27000	17000	25000	18000	74000	81000	62000
Si	mg/kg	180000	11000	8500	230000	110000	190000	83000	84000	100000	44000
Cl	mg/kg	6000	750	1800	4900	9200	2200	4000	5500	3300	10000
S	mg/kg	160000	9000	36000	91000	250000	44000	110000	56000	39000	92000
Mg	mg/kg	<31000	NR	NR	<25000	<46000	<21000	<43000	<34000	37000	57000

Sample Location	Units	BA-2	BA-2	BA-2	BA-2	BA-3	BA-3	BA-3	BA-3	BA-3
BA Fraction		Coarse (80%)	Fine (20%)	Coarse (65%)	Fine (35%)	Whole	Coarse (90%)	Fine (10%)	Coarse (80%)	Fine (20%)
Sample ID Number		15KK01545	15KK01544	15KK01851	15KK01850	15KK1175	15KK01583	15KK01580	15KK01582	15KK01581
TOC	%	1.6	1.1	NA	NA	0.51	0.56	0.9	0.67	0.78
Ca	mg/kg	200000	280000	170000	280000	190000	180000	250000	220000	220000
K	mg/kg	36000	45000	33000	43000	10000	9500	12000	13000	14000
P	mg/kg	16000	24000	10000	17000	5300	2900	5500	6100	8000
As	mg/kg	<4.6	4.7	<1.4	4.7	8.6	4.6	19	17	13
Ba	mg/kg	520	110	1300	2200	730	560	1100	1000	1000
Cd	mg/kg	5	16	4.7	15	1.7	<0.096	2.7	2.4	1.9
Cr	mg/kg	77	150	43	43	120	290	470	420	240
Cu	mg/kg	78	140	62	130	180	180	280	250	280
Hg	mg/kg	<0.10	0.19	<0.10	0.19	0.13	0.072	0.56	<0.040	0.5
Mo	mg/kg	6	18	3.7	7.9	5	12	37	33	14
Ni	mg/kg	53	110	30	43	88	170	260	240	130
Pb	mg/kg	19	39	39	67	20	20	53	48	48
V	mg/kg	29	21	28	23	27	25	27	24	25
Zn	mg/kg	2400	8400	1100	6300	310	280	830	740	780
XRF										
I	mg/kg	<12	<14	<12	<12	<11	<12	<13	<11	<12
Sb	mg/kg	<35	<40	<34	<40	<35	<33	<37	<33	<35
Sn	mg/kg	<36	<42	<34	<40	<34	<34	<37	<34	<36
Pd	mg/kg	30	81	<4.9	<5.8	<4.8	<4.9	<5.2	<4.6	<5.0
Ag	mg/kg	<87	<110	<71	<85	<110	<71	<79	<86	<87
Zr	mg/kg	300	150	340	190	140	150	110	190	110
Sr	mg/kg	410	610	370	570	420	400	550	390	500
Br	mg/kg	47	220	34	150	35	24	86	23	65
Se	mg/kg	<3.3	<5.9	<3.3	<4.8	<3.0	<3.3	<4.5	<2.9	<4.1
Tl	mg/kg	<9.1	<13	<8.5	<12	<8.5	<6.9	<10	<6.9	<9.2
Co	mg/kg	<120	<120	<120	<120	<110	<110	<110	<110	<110
Fe	mg/kg	18000	13000	18000	14000	14000	15000	14000	16000	14000
Mn	mg/kg	10000	19000	8000	17000	2900	2400	4900	2300	4700
Ti	mg/kg	3700	3200	4000	3500	2100	1900	2000	2000	2000
Al	mg/kg	81000	71000	66000	64000	69000	68000	72000	62000	74000
Si	mg/kg	99000	51000	96000	60000	170000	170000	140000	170000	160000
Cl	mg/kg	3200	8800	2800	6600	770	660	1300	610	980
S	mg/kg	38000	81000	37000	64000	19000	12000	30000	13000	23000
Mg	mg/kg	34000	56000	<25000	<40000	<24000	24000	<30000	<22000	<28000

Appendix D: Observed elemental distribution in air classified sample groups.

BA-1 90%/10%		
Coarse	No change or cannot be determined	Fine
Zr, Fe, Si	TOC, Ba, V, I, Sb, Sn, Pd, Ag, Se, Tl, Co, Ti, Al, Mg	Ca, K, P, As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Zn, Sr, Br, Mn, Cl, S

BA-1 81.5%/18.5%		
Coarse	No change or cannot be determined	Fine
Zr, Fe, Al, Si	TOC, V, I, Sb, Sn, Pd, Ag, Se, Tl, Co, Ti, Mg	Ca, K, P, As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Zn, Sr, Br, Mn, Cl, S

BA-1 65%/35%		
Coarse	No change or cannot be determined	Fine
Zr, Fe, Al, Si	Ba, V, I, Sb, Sn, Pd, Ag, Se, Tl, Co, Mg	Ca, K, P, As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Zn, Sr, Br, Mn, Ti, Cl, S

BA-2 90%/10%		
Coarse	No change or cannot be determined	Fine
TOC, Ba, Zr, Fe, Ti, Al, Si	Ca, V, I, Sb, Sn, Ag, Se, Tl, Co	K, P, As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Zn, Pd, Sr, Br, Mn, Cl, S, Mg

BA-2 80%/20%		
Coarse	No change or cannot be determined	Fine
TOC, Ba, Zr, Fe, Ti, Al, Si	V, I, Sb, Sn, Ag, Se, Tl, Co	Ca, K, P, As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Zn, Pd, Sr, Br, Mn, Cl, S, Mg

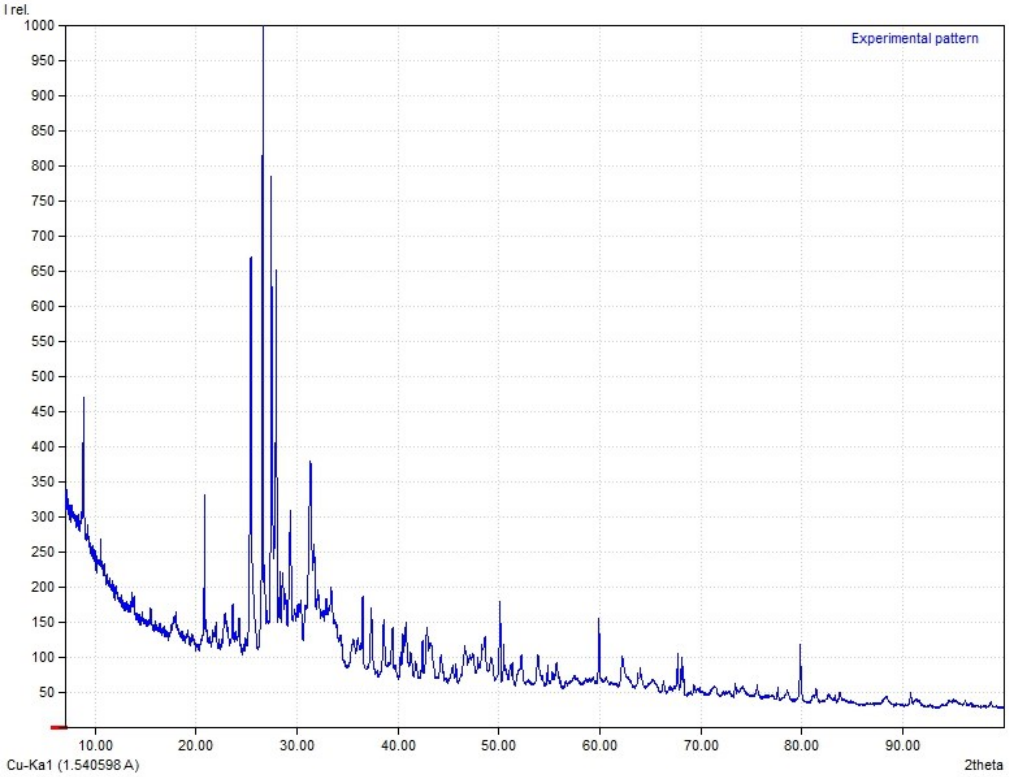
BA-2 65%/35%		
Coarse	No change or cannot be determined	Fine
Zr, Fe, Ti, Al, Si	Cr, V, I, Sb, Sn, Pd, Ag, Se, Tl, Co, Mg	Ca, K, P, As, Ba, Cd, Cu, Hg, Mo, Ni, Pb, Zn, Sr, Br, Mn, Cl, S

BA-3 90%/10%		
Coarse	No change or cannot be determined	Fine
Zr, Fe, Si	V, I, Sb, Sn, Pd, Ag, Se, Tl, Co, Ti, Al, Mg	TOC, Ca, K, P, As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Zn, Sr, Br, Mn, Cl, S

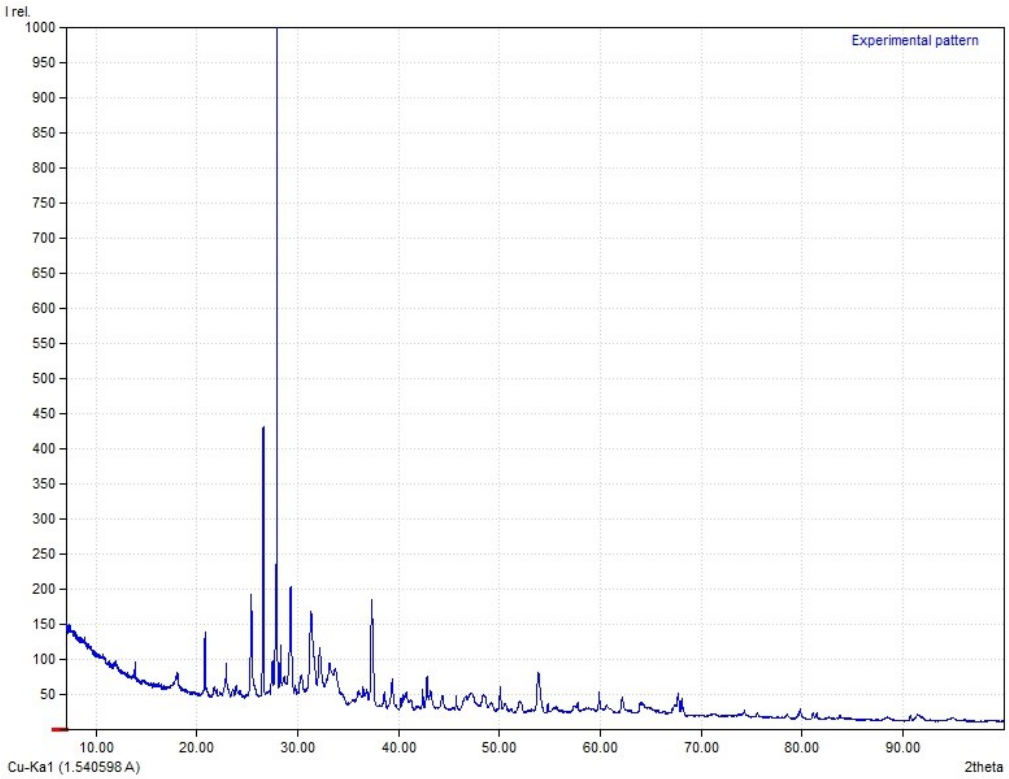
BA-3 80%/20%		
Coarse	No change or cannot be determined	Fine
Zr, Si, Cr, Mo, Ni	Ca, As, Ba, Cd, Cu, Pb, V, Zn, I, Sb, Sn, Pd, Ag, Se, Tl, Co, Fe, Ti, Al, Mg	TOC, K, P, Hg, Sr, Br, Mn, Cl, S

Appendix E: XRD Diffractograms

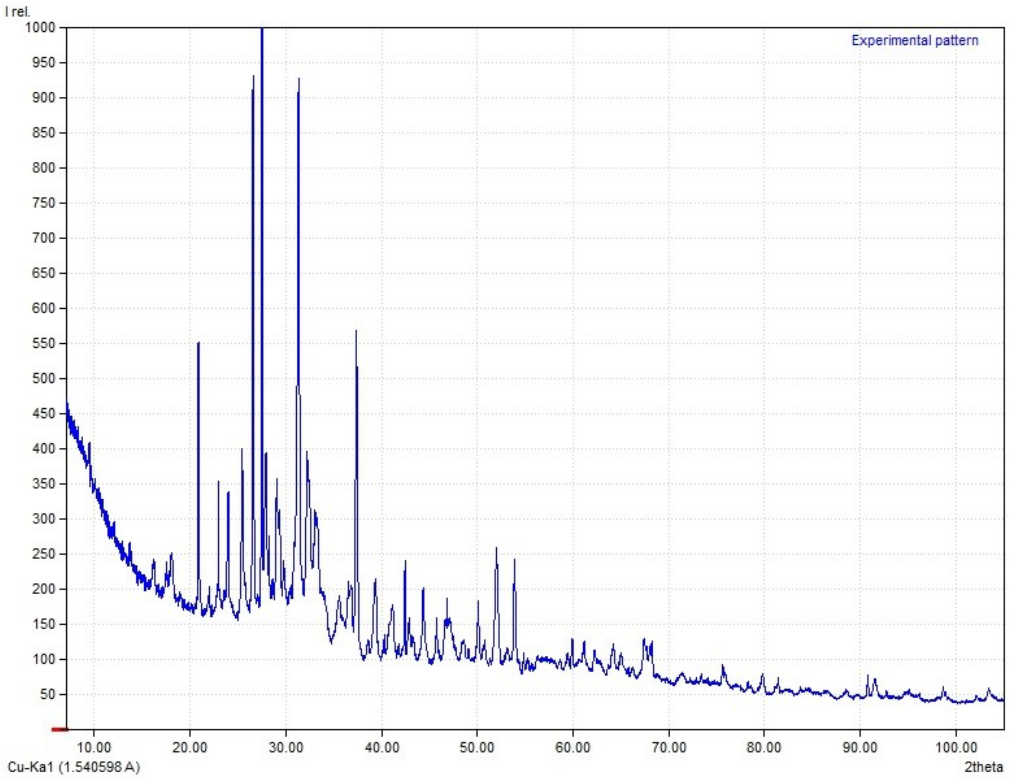
BA-1



BA-2



BA-3


I rel.
Experimental pattern
1000
950
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850
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60.00
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90.00
100.00
Cu-Ka1 (1.540598 A)
2theta

Appendix F: Data Tables for Fertilizer and Earth Construction

Macronutrient and heavy metal concentrations pertaining to agricultural and forestry fertilizers and limit values for use in agriculture and forestry in BA-1 and air classified samples.

Element	Unit	Agricultural ash-based fertilizers or raw materials added to ash	Forestry ash-based fertilizers or raw materials added to ash	Minimum or maximum elemental concentration	BA-1						
					Whole Sample	Coarse (90%)	Fine (10%)	Coarse (81.5%)	Fine (18.5%)	Coarse (65%)	Fine (35%)
Calcium (Ca)	%	10	6.0	min	13	14	25	11	21	11	25
Phosphorus (P)	%	-	-	-	1.3	1.2	2.2	2.7	5.3	0.82	2.2
Potassium (K)	%	-	-	-	3.3	3.5	6.9	1.0	2.4	3.5	6.3
P + K	%	2.0	2.0	min	4.6	4.7	9.1	3.7	7.7	4.32	8.5
Arsenic (As)	mg/kg	25	40	max	**62**	**49**	**140**	**36**	**140**	24	**120**
Cadmium (Cd)	mg/kg	2.5	25	max	**5.7**	**3.9**	**15**	**2.8**	**15**	1.9	**12**
Chromium (Cr)	mg/kg	300	300	max	110	**400**	**630**	220	**460**	170	**410**
Copper (Cu)	mg/kg	300	700	max	150	150	220	140	250	150	240
Mercury (Hg)	mg/kg	1.0	1.0	max	0.13	<0.10	0.24	<0.10	0.33	<0.10	0.34
Lead (Pb)	mg/kg	100	150	max	**130**	89	**240**	77	**260**	64	**220**
Nickel (Ni)	mg/kg	100	150	max	28	**220**	**360**	85	**190**	90	**230**
Zinc (Zn)	mg/kg	1500	4500	max	**2500**	**2200**	**4800**	**1800**	**4500**	**1600**	**4400**

BOLD indicates concentration exceeding upper or lower value for agriculture

indicates concentration exceeding upper or lower value for forestry

Total heavy metal concentrations pertaining to earth construction and limit values for use in earth construction in BA-1 and air classified samples.

Constituent	Limit value	BA-1						
		Whole Sample	Coarse (90%)	Fine (10%)	Coarse (81.5%)	Fine (18.5%)	Coarse (65%)	Fine (35%)
PCB	1.0	<0.07	NA	NA	NA	NA	NA	NA
PAH	20/40[1]	<3.0	NA	NA	NA	NA	NA	NA
Arsenic (As)	50	**62**	49	**140**	36	**140**	24	**120**
Barium (Ba)	3000	1600	230	130	1400	2600	1200	1200
Cadmium (Cd)	15	5.7	3.9	**15**	2.8	**15**	1.9	12
Chromium (Cr)	400	110	**400**	**630**	220	**460**	170	**410**
Copper (Cu)	400	150	150	220	140	250	150	240
Lead (Pb)	300	130	89	240	77	260	64	220
Molybdenum (Mo)	50	2.8	28	**55**	9.9	31	10	30
Vanadium (V)	400	35	29	28	35	39	28	33
Zinc (Zn)	2000	**2500**	**2200**	**4800**	1800	**4500**	1600	**4400**

[1] Covered structure/paved structure

BOLD indicates concentration exceeding limit value for use in earth construction

NA indicates sample not analyzed for specific constituent

All concentrations reported in mg/kg

Macronutrient and heavy metal concentrations pertaining to agricultural and forestry fertilizers and limit values for use in agriculture and forestry in BA-2 and air classified BA samples.

Element	Unit	Agricultural ash-based fertilizers or raw materials added to ash	Forestry ash-based fertilizers or raw materials added to ash	Minimum or maximum elemental concentration	BA-2						
					Whole Sample	Coarse (90%)	Fine (10%)	Coarse (80%)	Fine (20%)	Coarse (65%)	Fine (35%)
Calcium (Ca)	%	10	6.0	min	20	20	14	20	28	17	28
Phosphorus (P)	%	-	-	-	1.7	1.5	2.4	1.6	2.4	1.0	1.7
Potassium (K)	%	-	-	-	3.6	3.4	4.9	3.6	4.5	3.3	4.3
P + K	%	2.0	2.0	min	5.3	4.9	7.3	5.2	6.9	4.3	6
Arsenic (As)	mg/kg	25	40	max	3.6	<5.1	6.0	<4.6	4.7	<1.4	4.7
Cadmium (Cd)	mg/kg	2.5	25	max	**6.6**	**5.5**	**18**	**5.0**	**16**	**4.7**	**15**
Chromium (Cr)	mg/kg	300	300	max	55	150	**310**	77	150	43	43
Copper (Cu)	mg/kg	300	700	max	76	82	140	78	140	62	130
Mercury (Hg)	mg/kg	1.0	1.0	max	<0.10	0.19	0.29	<0.10	<0.10	<0.10	0.19
Lead (Pb)	mg/kg	100	150	max	19	20	45	19	39	39	67
Nickel (Ni)	mg/kg	100	150	max	34	91	**190**	53	**110**	30	43
Zinc (Zn)	mg/kg	1500	4500	max	**2200**	**2600**	**7700**	**2400**	**8400**	1100	**6300**

BOLD indicates concentration exceeding upper or lower value for agriculture

indicates concentration exceeding upper or lower value for forestry

Total heavy metal concentrations pertaining to earth construction and limit values for use in earth construction in BA-2 and air classified BA samples.

Constituent	Limit value	BA-2						
		Whole Sample	Coarse (90%)	Fine (10%)	Coarse (80%)	Fine (20%)	Coarse (65%)	Fine (35%)
PCB	1.0	<0.07	NA	NA	NA	NA	NA	NA
PAH	20/40[1]	<3.0	NA	NA	NA	NA	NA	NA
Arsenic (As)	50	3.6	<5.1	6	<4.6	4.7	<1.4	4.7
Barium (Ba)	3000	2000	1500	140	520	110	1300	2200
Cadmium (Cd)	15	6.6	5.5	**18**	5	**16**	4.7	**15**
Chromium (Cr)	400	55	150	310	77	150	43	43
Copper (Cu)	400	76	82	140	78	140	62	130
Lead (Pb)	300	19	20	45	19	39	39	67
Molybdenum (Mo)	50	3.8	11	33	6	18	3.7	7.9
Vanadium (V)	400	29	28	20	29	21	28	23
Zinc (Zn)	2000	**2200**	**2600**	**7700**	**2400**	**8400**	1100	**6300**

[1] Covered structure/paved structure

BOLD indicates concentration exceeding limit value for use in earth construction

NA indicates sample not analyzed for specific constituent

All concentrations reported in mg/kg

Macronutrient and heavy metal concentrations pertaining to agricultural and forestry fertilizers and limit values for use in agriculture and forestry in BA-3 and air classified samples.

Element	Unit	Agricultural ash-based fertilizers or raw materials added to ash	Forestry ash-based fertilizers or raw materials added to ash	Minimum or maximum elemental concentration	BA-3				
					Whole Sample	Coarse (90%)	Fine (10%)	Coarse (80%)	Fine (20%)
Calcium (Ca)	%	10	6.0	min	19	18	25	22	22
Phosphorus (P)	%	-	-	-	0.53	0.29	0.55	0.61	0.8
Potassium (K)	%	-	-	-	1.0	0.95	1.2	1.3	1.4
P + K	%	2.0	2.0	min	**1.53**	**1.24**	**1.75**	**1.91**	2.2
Arsenic (As)	mg/kg	25	40	max	8.6	4.6	19	17	13
Cadmium (Cd)	mg/kg	2.5	25	max	1.7	<0.096	**2.7**	2.4	1.9
Chromium (Cr)	mg/kg	300	300	max	120	290	**470**	**420**	240
Copper (Cu)	mg/kg	300	700	max	180	180	280	250	280
Mercury (Hg)	mg/kg	1.0	1.0	max	0.13	0.072	0.56	<0.040	0.52
Lead (Pb)	mg/kg	100	150	max	20	20	53	48	48
Nickel (Ni)	mg/kg	100	150	max	88	**170**	**260**	**240**	**130**
Zinc (Zn)	mg/kg	1500	4500	max	310	280	830	740	780

BOLD indicates concentration exceeding upper or lower value for agriculture

indicates concentration exceeding upper or lower value for forestry

Total heavy metal concentrations pertaining to earth construction and limit values for use in earth construction in BA-3 and air classified samples.

Constituent	Limit value	BA-3				
		Whole Sample	Coarse (90%)	Fine (10%)	Coarse (80%)	Fine (20%)
PCB	1.0	<0.07	NA	NA	NA	NA
PAH	20/40[1]	<3.0	NA	NA	NA	NA
Arsenic (As)	50	8.6	4.6	19	17	13
Barium (Ba)	3000	730	560	1100	1000	1000
Cadmium (Cd)	15	1.7	<0.096	2.7	2.4	1.9
Chromium (Cr)	400	120	290	**470**	**420**	240
Copper (Cu)	400	180	180	280	250	280
Lead (Pb)	300	20	20	53	48	48
Molybdenum (Mo)	50	5.0	12	37	33	14
Vanadium (V)	400	27	25	27	24	25
Zinc (Zn)	2000	310	280	830	740	780

[1] Covered structure/paved structure

BOLD indicates concentration exceeding limit value for use in earth construction

NA indicates sample not analyzed for specific constituent

All concentrations reported in mg/kg

Appendix G: Mass balance calculation for air classified samples exhibiting increases in specific metals concentrations

BA-1

Mass % Increase

	Sample (g)	Sample (kg)	Cr (mg/kg)	Mass Cr (mg)	Ni (mg/kg)	Mass Ni (mg)	Mo (mg/kg)	Mass Mo (mg)
Total In	345.3	0.3453	110	37.983	28	9.668	5.12	1.768
Coarse 81.5%	246.1	0.2461	220	54.142	85	20.919	9.9	2.436
Fine 18.5%	55.6	0.0556	460	25.576	190	10.564	31	1.724
Unrecovered	39.8	0.0398	110	4.378	28	1.114	5.12	0.204
Unclassified	3.8	0.0038	110	0.418	28	0.106	5.12	0.019
Total Out (mg)				84.514		32.703		4.383
% Increase				122.505		238.249		147.929
Total In	507.8	0.5078	110	55.858	28	14.218	2.8	1.422
Coarse 90%	412.6	0.4126	400	165.040	220	90.772	28	11.553
Fine 10%	43.6	0.0436	630	27.468	360	15.696	55	2.398
Unrecovered	46.2	0.0462	110	5.082	28	1.294	2.8	0.129
Unclassified	5.4	0.0054	110	0.594	28	0.151	2.8	0.015
Total Out (mg)				198.184		107.913		14.095
% Increase				254.800		658.966		891.341
Total In	201	0.201	110	22.110	28	5.628	2.8	0.563
Coarse 65%	121.1	0.1211	170	20.587	90	10.899	10	1.211
Fine 35%	67.1	0.0671	410	27.511	230	15.433	30	2.013
Unrecovered	6.9	0.0069	110	0.759	28	0.193	2.8	0.019
Unclassified	5.9	0.0059	110	0.649	28	0.165	2.8	0.017
Total Out (mg)				49.506		26.690		3.260
% Increase				123.908		374.243		479.218

Estimated Concentrations of Cr, Ni and Mo

	Est Cr	Est Ni	Est Mo
Classified Mass (mg)	33.2	8.4	1.5
Coarse 81.5% (mg/kg)	91.6	22.8	3.7
Fine 18.5% (mg/kg)	191.5	51.0	11.3
Ratio C/F Theoretical	0.4782605	0.4473680	0.3289504
Ratio C/F	0.4782609	0.4473684	0.3193548
Total Out Theor (mg)	37.98	9.67	1.77
Total In (mg)	37.98	9.67	1.77
Classified Mass (mg)	50.2	12.8	1.3
Coarse 90% (mg/kg)	104.3	26.4	2.6
Fine 10% (mg/kg)	164.2	43.2	5.0
Ratio C/F Theoretical	0.6349199	0.6111117	0.5090906
Ratio C/F	0.6349206	0.6111111	0.5090909
Total Out Theor (mg)	55.86	14.22	1.42
Total In (mg)	55.86	14.22	1.42
Classified Mass (mg)	20.7	5.3	0.5
Coarse 65% (mg/kg)	73.2	18.0	1.6
Fine 35% (mg/kg)	176.5	46.0	4.9
Ratio C/F Theoretical	0.4146339	0.3913035	0.3333334
Ratio C/F	0.4146341	0.3913043	0.3333333
Total Out Theor (mg)	22.11	5.63	0.56
Total In (mg)	22.11	5.63	0.56

BA-2

Mass % Increase

	Sample (g)	Sample (kg)	Cr (mg/kg)	Mass Cr (mg)	Ni (mg/kg)	Mass Ni (mg)	Mo (mg/kg)	Mass Mo (mg)
Total In	538.2	0.5382	55	29.601	34	18.299	3.8	2.045
Coarse 90%	428.6	0.4286	150	64.290	91	39.003	11	4.715
Fine 10%	47.6	0.0476	310	14.756	190	9.044	33	1.571
Unrecovered	38	0.038	55	2.090	34	1.292	3.8	0.144
Unclassified	24	0.024	55	1.320	34	0.816	3.8	0.091
Total Out (mg)				82.456		50.155		6.521
% Increase				178.558		174.087		218.850
Total In	247.1	0.2471	55	13.591	34	8.401	3.8	0.939
Coarse 80%	188.9	0.1889	77	14.545	53	10.012	6	1.133
Fine 20%	48.5	0.0485	150	7.275	110	5.335	18	0.873
Unrecovered	7.4	0.0074	55	0.407	34	0.252	3.8	0.028
Unclassified	2.3	0.0023	55	0.127	34	0.078	3.8	0.009
Total Out (mg)				22.354		15.677		2.043
% Increase				64.481		86.594		117.604
Total In	210.5	0.2105	55	11.578	34	7.157	3.8	0.800
Coarse 65%	125.7	0.1257	43	5.405	30	3.771	3.7	0.465
Fine 35%	70.6	0.0706	43	3.036	43	3.036	7.9	0.558
Unrecovered	6.3	0.0063	55	0.347	34	0.214	3.8	0.024
Unclassified	7.9	0.0079	55	0.435	34	0.269	3.8	0.030
Total Out (mg)				9.222		7.290		1.077
% Increase				-20.346		1.853		34.616

Estimated Concentrations of Cr, Ni and Mo

	Est Cr	Est Ni	Est Mo
Classified Mass (mg)	26.2	16.2	1.8
Coarse 90% (mg/kg)	49.7	30.7	3.2
Fine 10% (mg/kg)	102.7	64.0	9.5
Ratio C/F Theoretical	0.4838714	0.4789471	0.3333333
Ratio C/F	0.4838710	0.4789474	0.3333333
Total Out Theor (mg)	29.60	18.30	2.05
Total In (mg)	29.6	18.3	2.0
Classified Mass (mg)	13.1	8.1	0.9
Coarse 80% (mg/kg)	46.1	27.9	2.7
Fine 20% (mg/kg)	89.76	57.85	8.09
Ratio C/F Theoretical	0.5133334	0.4818179	0.3333340
Ratio C/F	0.5133333	0.4818182	0.3333333
Total Out Theor (mg)	13.59	8.40	0.94
Total In (mg)	13.59	8.40	0.94
Classified Mass (mg)	10.8	6.7	0.7
Coarse 80% (mg/kg)	55.0	29.4	2.7
Fine 20% (mg/kg)	55.00	42.16	5.76
Ratio C/F Theoretical	1.0000004	0.6976746	0.4683540
Ratio C/F	1.0000000	0.6976744	0.4683544
Total Out Theor (mg)	11.58	7.16	0.80
Total In (mg)	11.58	7.16	0.80

BA-3

Mass % Increase

	Sample (g)	Sample (kg)	Cr (mg/kg)	Mass Cr (mg)	Ni (mg/kg)	Mass Ni (mg)	Mo (mg/kg)	Mass Mo (mg)
Total In	555.3	0.5553	120	66.636	88	48.866	5	2.777
Coarse 90%	478.2	0.4782	290	138.678	170	81.294	12	5.738
Fine 10%	53.3	0.0533	470	25.051	260	13.858	37	1.972
Unrecovered	20.7	0.0207	120	2.484	88	1.822	5	0.104
Unclassified	3.1	0.0031	120	0.372	88	0.273	5	0.016
Total Out (mg)				166.585		97.246		7.830
% Increase				149.992		99.005		181.992
Total In	269	0.269	120	32.280	88	23.672	5	1.345
Coarse 80%	207.4	0.2074	420	87.108	240	49.776	33	6.844
Fine 20%	54.3	0.0543	240	13.032	130	7.059	14	0.760
Unrecovered	5.6	0.0056	120	0.672	88	0.493	5	0.028
Unclassified	1.7	0.0017	120	0.204	88	0.150	5	0.009
Total Out (mg)				101.016		57.477		7.641
% Increase				212.937		142.808		468.097

Estimated Concentrations of Cr, Ni and Mo

	Est Cr	Est Ni	Est Mo
Classified Mass (mg)	63.8	46.8	2.7
Coarse 90% (mg/kg)	113.0	83.6	4.1
Fine 10% (mg/kg)	183.1	127.8	12.8
Ratio C/F Theoretical	0.6170205	0.6538455	0.3243235
Ratio C/F	0.6170213	0.6538462	0.3243243
Total Out Theor (mg)	66.64	48.87	2.78
Total In (mg)	66.64	48.87	2.78
Classified Mass (mg)	31.4	23.0	1.3
Coarse 80% (mg/kg)	131.7	97.2	5.7
Fine 20% (mg/kg)	75.3	52.7	2.4
Ratio C/F Theoretical	1.7499993	1.8461542	2.3571432
Ratio C/F	1.7500000	1.8461538	2.3571429
Total Out Theor (mg)	32.28	23.672	1.345
Total In (mg)	32.28	23.672	1.345